Chapter 1

Perturbation theory

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It is often the case that the Hamiltonian of a system differs slightly from a Hamiltonian that is well studied and completely understood. This is a situation where perturbation theory can be useful. Perturbation theory allows us to make statements about the Hamiltonian of the system using what we know about the well studied Hamiltonian.

The well studied Hamiltonian could be the that of the simple harmonic oscillator in one, two, or three dimensions. In a diatomic molecule, for example, the potential that controls the vibrations is not exactly quadratic; it has extra terms that make the vibrations slightly anharmonic. In that situation the extra terms in the potential represent perturbations of the Hamiltonian. The hydrogen atom Hamiltonian is also a well understood system. If we place the atom inside a weak external magnetic field or electric field, the situation is described by adding some small terms to the hydrogen Hamiltonian. Similarly, the interaction between the magnetic moments of the proton and the electron can be incorporated by modifying the original hydrogen atom Hamiltonian. The interaction between two neutral hydrogen atoms at a distance, leading to the van der Waals force can be studied in perturbation theory by thinking of the two atoms as electric dipoles.

The Hamiltonian of interest is written as the understood, original Hamiltonian $H^{(0)}$, plus a perturbation δH:

$$H^{(0)} + \delta H\,. \tag{1.0.1}$$

Since $H^{(0)}$ is Hermitian and the sum must be a Hermitian Hamiltonian, the perturbation operator δH must also be Hermitian. It is convenient to introduce a unit-free constant $\lambda \in [0,1]$ and to consider, instead, a λ-dependent Hamiltonian $H(\lambda)$ that takes the form

$$H(\lambda) \;=\; H^{(0)} + \lambda\,\delta H\,. \tag{1.0.2}$$

When $\lambda = 1$ we have the Hamiltonian of interest, but λ allows us to consider a family of Hamiltonians that interpolate from $H^{(0)}$, when λ is equal to zero, to the Hamiltonian of interest for λ equal to one. In many cases perturbations can be turned on and off; think,

for example, of an atom in an external magnetic field that can be varied continuously. In that case we can view λ as the parameter that allows us to turn on the perturbation by letting $\lambda \neq 0$. The parameter λ is also useful in organizing the perturbation analysis, as we will see below.

We spoke of a Hamiltonian that differs slightly from $H^{(0)}$. In order to use perturbation theory we need $\lambda\delta H$ to be a 'small' perturbation of the Hamiltonian $H^{(0)}$. We will have to deal with the meaning of small. At first sight we may imagine that small means that, viewed as matrices, the largest entries in $\lambda\delta H$ are smaller than the largest entries in $H^{(0)}$. While this is necessary, more is needed, as we will see in our analysis. An additional advantage of using λ is that by taking it to be sufficiently small we can surely make $\lambda\delta H$ small.

We assume that the Hamiltonian $H^{(0)}$ is understood, namely, we know the eigenstates and eigenvalues of $H^{(0)}$. We want to know the eigenstates and eigenvalues of $H(\lambda)$. One may be able to calculate those exactly, but this is seldom a realistic possibility. Diagonalizing δH is seldom useful, since δH and H do not generally commute and therefore δH eigenstates are not eigenstates of $H(\lambda)$. In perturbation theory the key assumption is that the eigenvalues and eigenvectors of $H(\lambda)$ can be found as series expansions in powers of λ. We hope, of course, that there are some values of λ for which the series converges, or at least gives useful information.

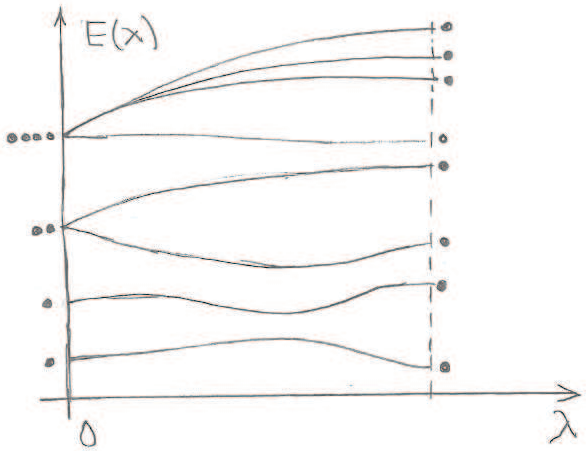

Figure 1.1: The energy eigenvalues of $H(\lambda)$ as λ varies from zero to one. On the $\lambda = 0$ vertical axis the $H^{(0)}$ eigenstates are represented by heavy dots. By the time $\lambda = 1$ the dots have shifted.

In Figure 1.1 we illustrate some of the phenomena that we may see in the spectrum of a system with Hamiltonian $H(\lambda)$. We show how the energies of the various states may change as the parameter λ is increased from zero. The two lowest energy eigenstates are non-degenerate and their energies can go up and down as λ varies. Next up in energy we have two degenerate states of $H^{(0)}$ (the Hamiltonian as $\lambda = 0$). The perturbation splits the

two levels, and that happens generically. In the figure, the perturbation splits the levels to first order in λ, as shown by the different slopes of the two curves that meet at $\lambda = 0$. In other words, viewed as power series in λ the energies of the two states have different linear terms in λ. The last level shown corresponds to four degenerate states. The perturbation to first order in λ splits the states into a group of three states and a fourth. To second order in λ the three states split further. A single Hamiltonian can exhibit behavior like this, with many possible variations.

To analyze the evolution of states and energies as functions of λ we have two possible cases: (i) we are following a non-degenerate state or, (ii) we are following a collection of degenerate states. The challenges are quite different and therefore we must analyze them separately. Clearly both situations can occur for a single Hamiltonian, depending on the spectrum of $H^{(0)}$. To follow a non-degenerate state we use *non-degenerate perturbation theory*. To follow a set of degenerate states we use *degenerate perturbation theory*. Since Hamiltonians $H^{(0)}$ generally have both non-degenerate and degenerate states we need to consider both types of perturbation theory. We begin with non-degenerate perturbation theory.

1.1 Nondegenerate perturbation theory

We begin by describing the original Hamiltonian $H^{(0)}$. We assume this Hamiltonian has a discrete spectrum with an orthonormal basis $|k^{(0)}\rangle$ of energy eigenstates, where $k \in \mathbb{Z}$ is a label that ranges over a possibly infinite set of values:

$$H^{(0)}\,|k^{(0)}\rangle \;=\; E_k^{(0)}\,|k^{(0)}\rangle\,, \quad \langle k^{(0)}|l^{(0)}\rangle \;=\; \delta_{kl}\,. \tag{1.1.1}$$

We will let $k = 0$ denote the ground state and we order the states so that the energies generally increase as the value of the label increases, so that

$$E_0^{(0)} \;\leq\; E_1^{(0)} \;\leq\; E_2^{(0)} \;\leq\; E_3^{(0)} \;\leq\; \ldots \tag{1.1.2}$$

The equal signs are needed because some states may be degenerate.

In this section we focus on a non-degenerate state $|n^{(0)}\rangle$ with fixed n. This means that $|n^{(0)}\rangle$ is a single state that is separated by some finite energy from all the states with more energy and from all the states with less energy. In other words the following must be part of the sequence of inequalities in (1.1.2)

$$\ldots \;\leq\; E_{n-1}^{(0)} \;<\; E_n^{(0)} \;<\; E_{n+1}^{(0)} \;\leq\; \ldots \tag{1.1.3}$$

If the chosen state is the ground state, we have instead $E_0^{(0)} \;<\; E_1^{(0)}$.

As the perturbation is turned on by making λ different from zero, the energy eigenstate $|n^{(0)}\rangle$ of $H^{(0)}$ will evolve into some energy eigenstate $|n\rangle_\lambda$ of $H(\lambda)$ with energy $E_n(\lambda)$:

$$H(\lambda)|n\rangle_\lambda \;=\; E_n(\lambda)\,|n\rangle_\lambda\,, \tag{1.1.4}$$

where

$$|n\rangle_{\lambda=0} \;=\; |n^{(0)}\rangle\,, \quad \text{and} \quad E_n(\lambda=0) \;=\; E_n^{(0)}\,. \tag{1.1.5}$$

As we said, the solution is assumed to take the form of a regular power series expansion in λ. To make this clear consider a function $f(\lambda)$ such that its derivatives to all orders exist for $\lambda = 0$. In that case we have a Taylor expansion

$$f(\lambda) = \sum_{n=0}^{\infty} \frac{1}{n!} f^{(n)}(0)\,\lambda^n \;=\; f(0) + f'(0)\,\lambda + \tfrac{1}{2} f''(0)\,\lambda^2 + \tfrac{1}{3!} f'''(0)\,\lambda^3 + \cdots \tag{1.1.6}$$

The expansion is a power series in λ, with coefficients $f(0), f'(0)$, etc, that are λ independent and reflect the value of the function and its derivatives at $\lambda = 0$.

For our problem we note the values of $|n\rangle_\lambda$ and $E_n(\lambda)$ for $\lambda = 0$ (1.1.5) and write:

$$\begin{aligned} |n\rangle_\lambda \;&=\; |n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \lambda^3|n^{(3)}\rangle + \dots\,, \\ E_n(\lambda) \;&=\; E_n^{(0)} \;+\lambda\, E_n^{(1)} \;+\lambda^2\, E_n^{(2)} \;+\lambda^3\, E_n^{(3)} \;+\dots \end{aligned} \tag{1.1.7}$$

The superscripts on the states and energies denote the power of λ that accompanies them in the above expressions. The above equations are a natural assumption; they state that the perturbed states and energies, being functions of λ, admit a Taylor expansion around $\lambda = 0$. Our aim is to calculate the states

$$|n^{(1)}\rangle\,, \quad |n^{(2)}\rangle\,, \quad |n^{(3)}\rangle\,, \dots \tag{1.1.8}$$

and the energies

$$E_n^{(1)}\,, \quad E_n^{(2)}\,, \quad E_n^{(3)}\,, \quad \dots \tag{1.1.9}$$

Note that all these states and energies are, by definition, λ independent. Here $|n^{(1)}\rangle$ is the leading correction to the state $|n^{(0)}\rangle$ as we turn on λ, and $E_n^{(1)}$ is the leading correction to the energy as we turn on λ. We will *not* impose the requirement that $|n\rangle_\lambda$ is normalized. It suffices that $|n\rangle_\lambda$ is normalizable, which it will be for sufficiently small perturbations. For $\lambda = 1$ we would find the solution for $H(1) = H^{(0)} + \delta H$ in the form

$$\begin{aligned} |n\rangle \equiv\; |n\rangle_1 \;&=\; |n^{(0)}\rangle + |n^{(1)}\rangle + |n^{(2)}\rangle + |n^{(3)}\rangle + \dots\,, \\ E_n \equiv\; E_n(1) \;&=\; E_n^{(0)} \;+\; E_n^{(1)} \;+\; E_n^{(2)} \;+\; E_n^{(3)} \;+\dots \end{aligned} \tag{1.1.10}$$

Substituting the ansatz (1.1.7) into the Schrödinger equation (1.1.4) we will find the conditions for such solution to exist:

$$\big(H^{(0)} + \lambda\delta H - E_n(\lambda)\big)|n\rangle_\lambda \;=\; 0\,, \tag{1.1.11}$$

which more explicitly takes the form

$$\begin{aligned} \Big((H^{(0)} - E_n^{(0)}) - \lambda(E_n^{(1)} - \delta H) - \lambda^2 E_n^{(2)} - \lambda^3 E_n^{(3)} - \dots - \lambda^k\, E_n^{(k)} + \dots\Big) \\ \Big(|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \lambda^3|n^{(3)}\rangle + \dots + \lambda^k|n^{(k)}\rangle + \dots\Big) \;=\; 0\,. \end{aligned} \tag{1.1.12}$$

Multiplying out we get a series in λ with coefficients λ-independent vectors in the state space of the theory. If this is to vanish for all values of λ those coefficients must be zero. Collecting the coefficients for each power of λ we

$$\boxed{\begin{aligned}
\lambda^0 :&\quad (H^{(0)}-E_n^{(0)})\,|n^{(0)}\rangle \;=\; 0\,,\\
\lambda^1 :&\quad (H^{(0)}-E_n^{(0)})\,|n^{(1)}\rangle \;=\; (E_n^{(1)}-\delta H)|n^{(0)}\rangle\,,\\
\lambda^2 :&\quad (H^{(0)}-E_n^{(0)})\,|n^{(2)}\rangle \;=\; (E_n^{(1)}-\delta H)|n^{(1)}\rangle \,+\, E_n^{(2)}\,|n^{(0)}\rangle\,,\\
\lambda^3 :&\quad (H^{(0)}-E_n^{(0)})\,|n^{(3)}\rangle \;=\; (E_n^{(1)}-\delta H)|n^{(2)}\rangle \,+\, E_n^{(2)}\,|n^{(1)}\rangle \,+E_n^{(3)}\,|n^{(0)}\rangle\,,\\
&\;\;\vdots \qquad\quad \vdots\quad \vdots\\
\lambda^k :&\quad (H^{(0)}-E_n^{(0)})\,|n^{(k)}\rangle \;=\; (E_n^{(1)}-\delta H)|n^{(k-1)}\rangle \,+\, E_n^{(2)}\,|n^{(k-2)}\rangle+\ldots+E_n^{(k)}\,|n^{(0)}\rangle\,.
\end{aligned}} \tag{1.1.13}$$

Each equation is the condition that the coefficient multiplying the power of λ indicated to the left vanishes. That power is reflected as the sum of superscripts on each term, counting δH as having superscript one. This gives a simple consistency check on our equations. These are equations for the kets $|n^{(1)}\rangle, |n^{(2)}\rangle, \ldots$ as well as the energy corrections $E_n^{(1)}, E_n^{(2)}, \ldots$. Note again that λ does not enter into the equations, and thus the kets and energy corrections are λ independent.

The first equation, corresponding to λ^0, is satisfied by construction. The second equation, corresponding to λ^1, should allow us to solve for the first correction $|n^{(1)}\rangle$ to the state and the first correction $E_n^{(1)}$ to the energy. Once these are known, the equation corresponding to λ^2 involves only the unknowns $|n^{(2)}\rangle$ and $E_n^{(2)}$, and should determine them. At each stage each equation has only two unknowns: a state correction $|n^{(k)}\rangle$ and an energy correction $E_n^{(k)}$.

A useful choice. We now claim that without loss of generality we can assume that all the state corrections $|n^k\rangle$, with $k \geq 1$ contain no vector along $|n^{(0)}\rangle$. Explicitly:

$$\boxed{0 \;=\; \langle n^{(0)}|n^{(1)}\rangle \;=\; \langle n^{(0)}|n^{(2)}\rangle \;=\; \langle n^{(0)}|n^{(3)}\rangle \;=\; \ldots\,.} \tag{1.1.14}$$

To show this we explain how we can manipulate a solution that does not have this property into one that does. Suppose you have solution in which the state corrections $|n^{(k)}\rangle$ have components along $|n^{(0)}\rangle$:

$$|n^{(k)}\rangle = |n^{(k)}\rangle' - a_k|n^{(0)}\rangle, \quad k\geq 1\,, \tag{1.1.15}$$

with some constants a_k and with $|n^{(k)}\rangle'$ orthogonal to $|n^{(0)}\rangle$. Then the solution for the full

corrected state is

$$\begin{aligned} |n\rangle_\lambda &= |n^{(0)}\rangle + \lambda\left(|n^{(1)}\rangle' - a_1|n^{(0)}\rangle\right) + \lambda^2\left(|n^{(2)}\rangle' - a_2|n^{(0)}\rangle\right) + \dots \\ &= \left(1 - a_1\lambda - a_2\lambda^2 - \dots\right)|n^{(0)}\rangle + \lambda|n^{(1)}\rangle' + \lambda^2|n^{(2)}\rangle' + \dots \end{aligned} \tag{1.1.16}$$

Since this is an eigenstate of the Hamiltonian $H(\lambda)$, it will still be an eigenstate if we change its normalization by dividing it by any function of λ. Dividing by the coefficient of $|n^{(0)}\rangle$ we have the physically identical solution $|n\rangle'_\lambda$ given by

$$|n\rangle'_\lambda = |n^{(0)}\rangle + \frac{1}{\left(1 - a_1\lambda - a_2\lambda^2 - \dots\right)}\left[\lambda|n^{(1)}\rangle' + \lambda^2|n^{(2)}\rangle' + \dots\right] \tag{1.1.17}$$

We can expand the denominator so that we get

$$|n\rangle'_\lambda = |n^{(0)}\rangle + \lambda|n^{(1)}\rangle' + \lambda^2\left(|n^{(2)}\rangle' + a_1|n^{(1)}\rangle'\right) + \dots \tag{1.1.18}$$

The explicit expressions do not matter, the key point, actually visible in (1.1.17), is that we have a physically identical solution of the same equation in which the state corrections are all orthogonal to $|n^{(0)}\rangle$. This shows that we can impose the conditions (1.1.14) without loss of generality.

Solving the equations. Let us finally begin solving equations (1.1.13). For this we note that the Schrodinger equation for the ket $|n^{(0)}\rangle$ implies that for the bra we have

$$\langle n^{(0)}|(H^{(0)} - E_n^{(0)}) = 0\,. \tag{1.1.19}$$

This means that acting with $\langle n^{(0)}|$ on the left-hand side of any of the equations in (1.1.13) will give zero. Consistency requires that acting with $\langle n^{(0)}|$ on the right-hand side of any of the equations in (1.1.13) also give zero, and presumably some interesting information. For the λ-equation this gives:

$$0 = \langle n^{(0)}|(E_n^{(1)} - \delta H)|n^{(0)}\rangle\,. \tag{1.1.20}$$

Since $|n^{(0)}\rangle$ is normalized and $E_n^{(1)}$ is a number, this means that

$$\boxed{E_n^{(1)} = \langle n^{(0)}|\delta H|n^{(0)}\rangle\,.} \tag{1.1.21}$$

This is the *most famous* result in perturbation theory: the first correction to the energy of an energy eigenstate is simply the expectation value of the correction to the Hamiltonian in the *uncorrected* state. You need not know the correction to the state to determine the first correction to the energy! Note that the hermicity of δH implies the required reality of the energy correction.

We can actually find some interesting formulae (but not yet fully explicit!) for the higher energy corrections. For the λ^2 equation, acting with $\langle n^{(0)}|$ on the right-hand side gives

$$0 = \langle n^{(0)}|\Big((E_n^{(1)} - \delta H)|n^{(1)}\rangle + E_n^{(2)}\,|n^{(0)}\rangle\Big)\,. \tag{1.1.22}$$

Recalling our orthogonality assumption, we have $\langle n^{(0)}|n^{(1)}\rangle = 0$ and the term with $E_n^{(1)}$ drops out. We get

$$E_n^{(2)} \;=\; \langle n^{(0)}|\delta H|n^{(1)}\rangle\,, \tag{1.1.23}$$

which states that the second correction to the energy is determined if we have the first correction $|n^{(1)}\rangle$ to the state. Note that this expression is not explicit enough to make it manifest that $E_n^{(2)}$ is real. This and the earlier result for the first correction to the energy have a simple generalization. Acting with $\langle n^{(0)}|$ on the last equation of (1.1.13) we get

$$0 \;=\; \langle n^{(0)}|\Big(\;(E_n^{(1)}-\delta H)|n^{(k-1)}\rangle \;+\; E_n^{(2)}\,|n^{(k-2)}\rangle + \ldots + E_n^{(k)}\,|n^{(0)}\rangle\Big)\,. \tag{1.1.24}$$

Using the orthogonality of $|n^{(0)}\rangle$ and all the state corrections, we have

$$0 \;=\; -\langle n^{(0)}|\delta H)|n^{k-1}\rangle \;+ E_n^{(k)}\,, \tag{1.1.25}$$

and therefore we have

$$\boxed{E_n^{(k)} \;=\; \langle n^{(0)}|\,\delta H\,|n^{(k-1)}\rangle\,.} \tag{1.1.26}$$

At any stage of the recursive solution, the energy at a fixed order is known if the state correction is known to previous order. So it is time to calculate the corrections to the states!

Let us solve for the first correction $|n^{(1)}\rangle$ to the state. This state must be some particular superposition of the original energy eigenstates $|k^{(0)}\rangle$. For this we look at the equation

$$(H^{(0)}-E_n^{(0)})\,|n^{(1)}\rangle \;=\; (E_n^{(1)}-\delta H)|n^{(0)}\rangle\,. \tag{1.1.27}$$

This is a vector equation: the left-hand side vector set equal to the right-hand side vector. As in any vector equation, we can check it using a basis set of vectors. Forming the inner product of each and every basis vector with both the left-hand side and the right-hand side, we must get equal numbers. We already acted on the above equation with $\langle n^{(0)}|$ to figure out $E_n^{(1)}$. The remaining information in this equation can be obtained by acting with all the states $\langle k^{(0)}|$ with $k\neq n$:

$$\langle k^{(0)}|(H^{(0)}-E_n^{(0)})\,|n^{(1)}\rangle \;=\; \langle k^{(0)}|(E_n^{(1)}-\delta H)|n^{(0)}\rangle\,. \tag{1.1.28}$$

On the left-hand side we can let $H^{(0)}$ act on the bra. On the right-hand side we note that with $k\neq n$ the term with $E_n^{(1)}$ vanishes

$$(E_k^{(0)}-E_n^{(0)})\,\langle k^{(0)}|\,n^{(1)}\rangle \;=\; -\langle k^{(0)}|\delta H|n^{(0)}\rangle\,. \tag{1.1.29}$$

To simplify notation we define the matrix elements of δH in the original basis

$$\delta H_{mn} \;\equiv\; \langle m^{(0)}|\delta H|n^{(0)}\rangle\,. \tag{1.1.30}$$

Note that the Hermiticity of δH implies that

$$\delta H_{nm} = (\delta H_{mn})^* \,. \tag{1.1.31}$$

With this notation, equation (1.1.29) gives

$$\langle k^{(0)} | \, n^{(1)} \rangle \;=\; - \frac{\delta H_{kn}}{E_k^{(0)} - E_n^{(0)}} \,, \qquad k \neq n \,. \tag{1.1.32}$$

Since we now know the overlap of $|n^{(1)}\rangle$ with all basis states, this means that the state has been determined. Indeed we can use the completeness of the basis to write

$$|n^{(1)}\rangle \;=\; \sum_k |k^{(0)}\rangle\langle k^{(0)}|n^{(1)}\rangle = \sum_{k\neq n} |k^{(0)}\rangle\langle k^{(0)}|n^{(1)}\rangle \,, \tag{1.1.33}$$

since the term with $k = n$ does not contribute because of the orthogonality assumption. Using the overlaps (1.1.32) we now get

$$\boxed{|n^{(1)}\rangle \;=\; - \sum_{k\neq n} \frac{|k^{(0)}\rangle \delta H_{kn}}{E_k^{(0)} - E_n^{(0)}} \,.} \tag{1.1.34}$$

This shows that the first correction $|n^{(1)}\rangle$ can have components along all basis states, except $|n^{(0)}\rangle$. The component along a state $|k^{(0)}\rangle$ vanishes if the perturbation δH does not couple $|n^{(0)}\rangle$ to $|k^{(0)}\rangle$, namely, if δH_{kn} vanishes. Note that the assumption of non-degeneracy is needed here. We are summing over all states $|k^{(0)}\rangle$ that are not $|n^{(0)}\rangle$ and if any such state has the same $H^{(0)}$ energy as $|n^{(0)}\rangle$ the energy denominator will vanish causing trouble!

Now that we have the first order correction to the states we can compute the *second order* correction to the energy. Using (1.1.23) we have

$$E_n^{(2)} \;=\; \langle n^{(0)}|\delta H|n^{(1)}\rangle \;=\; - \sum_{k\neq n} \frac{\langle n^{(0)}|\delta H|k^{(0)}\rangle \delta H_{kn}}{E_k^{(0)} - E_n^{(0)}} \,. \tag{1.1.35}$$

In the last numerator we have $\langle n^{(0)}|\delta H|k^{(0)}\rangle = \delta H_{nk} = (\delta H_{kn})^*$ and therefore

$$E_n^{(2)} \;=\; - \sum_{k\neq n} \frac{|\delta H_{kn}|^2}{E_k^{(0)} - E_n^{(0)}} \,. \tag{1.1.36}$$

This is the second-order energy correction. This explicit formula makes the reality of $E_n^{(2)}$ manifest.

In summary, going back to (1.1.7), we have that the states and energies for $H(\lambda) = H^{(0)} + \lambda \delta H$ are, to this order,

$$\boxed{\begin{aligned} |n\rangle_\lambda \;&=\; |n^{(0)}\rangle - \lambda \sum_{k\neq n} \frac{\delta H_{kn}}{E_k^{(0)} - E_n^{(0)}} \, |k^{(0)}\rangle + \mathcal{O}(\lambda^2) \,, \\ E_n(\lambda) \;&=\; E_n^{(0)} \;+ \lambda \, \delta H_{nn} \;- \lambda^2 \sum_{k\neq n} \frac{|\delta H_{kn}|^2}{E_k^{(0)} - E_n^{(0)}} \;+ \mathcal{O}(\lambda^3) \,, \end{aligned}} \tag{1.1.37}$$

Remarks:

1. The first order corrected energy of the (non-degenerate) ground state *overstates* the true exact ground state energy. To see this consider the first order corrected ground state energy $E_0^{(0)} + \lambda E_0^{(1)}$. Writing this in terms of expectation values, with $|0^{(0)}\rangle$ denoting the unperturbed ground state, we have

$$\begin{aligned} E_0^{(0)} + \lambda E_0^{(1)} &= \langle 0^{(0)}|H^{(0)}|0^{(0)}\rangle + \lambda\langle 0^{(0)}|\delta H|0^{(0)}\rangle \\ &= \langle 0^{(0)}|(H^{(0)} + \lambda\delta H)|0^{(0)}\rangle \\ &= \langle 0^{(0)}|H(\lambda)|0^{(0)}\rangle\,. \end{aligned} \tag{1.1.38}$$

   By the variational principle, the expectation value of the Hamiltonian on an arbitrary (normalized) state is larger than the ground state energy $E_0(\lambda)$, therefore

$$E_0^{(0)} + \lambda E_0^{(1)} \;=\; \langle 0^{(0)}|H(\lambda)|0^{(0)}\rangle \;\geq\; E_0(\lambda)\,, \tag{1.1.39}$$

   which is what we wanted to prove. Given this overestimate at first order, the second order correction to the ground state energy is always negative. Indeed,

$$-\lambda^2 \sum_{k\neq 0} \frac{|\delta H_{k0}|^2}{E_k^{(0)} - E_0^{(0)}}\,, \tag{1.1.40}$$

   and each term is negative because the unperturbed excited state energies $E_k^{(0)}$ $(k \neq 0)$ exceed the unperturbed ground state energy $E_0^{(0)}$.

2. The second order correction to the energy of the $|n^{(0)}\rangle$ eigenstate exhibits *level repulsion*: the levels with $k > n$ push the state down and the levels with $k < n$ push the state up. Indeed,

$$-\lambda^2 \sum_{k\neq n} \frac{|\delta H_{kn}|^2}{E_k^{(0)} - E_n^{(0)}} \;=\; -\lambda^2 \sum_{k>n} \frac{|\delta H_{kn}|^2}{E_k^{(0)} - E_n^{(0)}} + \lambda^2 \sum_{k<n} \frac{|\delta H_{kn}|^2}{E_n^{(0)} - E_k^{(0)}}\,. \tag{1.1.41}$$

   The first term gives the negative contribution from the higher energy states and the second term gives the contribution from the lower energy states (see Figure 1.2).

The systematics of solving the equations is now apparent. For each equation we take inner products with all states in the state space. That gives the full content of the equation. We first take the inner product with $\langle n^{(0)}|$, as this makes the left-hand side equal to zero and is thus simpler. Then we take the inner product with $\langle k^{(0)}|$ with all $k \neq n$ and that gives the remainder of the information that is contained in the equation.

Exercise 1. Calculate $|n^{(2)}\rangle$ and $E_n^{(3)}$.

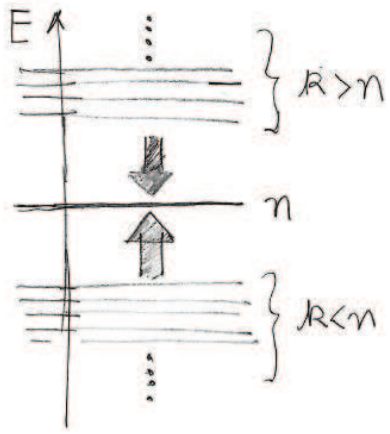

Figure 1.2: The second order corrections to the energy of the state $|n^{(0)}\rangle$ receives negative contributions from the higher energy states and positive contributions from the lower energy states. We have, effectively, a repulsion preventing the state $|n^{(0)}\rangle$ from approaching the neighboring states.

Exercise 2. The state $|n\rangle_\lambda$ is not normalized. Use (1.1.37) to calculate to order λ^2 the quantity $Z_n(\lambda)$ defined by

$$\frac{1}{Z_n(\lambda)} \equiv {}_\lambda\langle n|n\rangle_\lambda \ . \tag{1.1.42}$$

What is the probability that the state $|n\rangle_\lambda$ will be observed to be along its unperturbed version $|n^{(0)}\rangle$?

1.1.1 Validity of the perturbation expansion

We now return to a question we did not address: What do we mean when we say that $\lambda\delta H$ is small? We have said that $\lambda\delta H$ must be small compared to the original Hamiltonian $H^{(0)}$, but it is not clear what this means, as both expressions are operators. For some insight into this matter consider an example where $H^{(0)}$ is a two-by-two diagonal matrix with non-degenerate eigenvalues

$$H^{(0)} = \begin{pmatrix} E_1^{(0)} & 0 \\ 0 & E_2^{(0)} \end{pmatrix} . \tag{1.1.43}$$

The perturbation, called $\lambda\hat{V}$, only has off-diagonal elements so that

$$H(\lambda) \ = \ H^{(0)} + \lambda\hat{V} \equiv \begin{pmatrix} E_1^{(0)} & \lambda V \\ \lambda V^* & E_2^{(0)} \end{pmatrix} . \tag{1.1.44}$$

In this simple example there is no need to use perturbation theory since the eigenvalues, E_+ and E_-, can be calculated exactly as functions of λ

$$E_\pm(\lambda) \;=\; \tfrac{1}{2}(E_1^{(0)} + E_2^{(0)}) \;\pm\; \tfrac{1}{2}(E_1^{(0)} - E_2^{(0)})\sqrt{1 + \left[\frac{\lambda|V|}{\frac{1}{2}(E_1^{(0)} - E_2^{(0)})}\right]^2}\,. \tag{1.1.45}$$

The perturbative expansion of the energies is obtained by Taylor expansion of the square

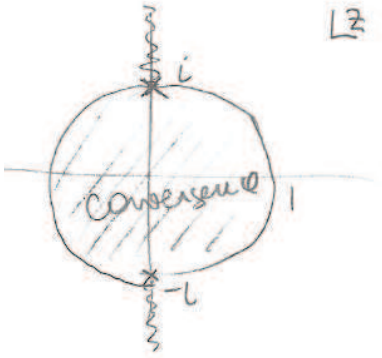

Figure 1.3: The Taylor expansion of the function $f(z) = \sqrt{1+z^2}$ about $z = 0$ has a radius of convergence equal to one.

root in powers of λ. To perform this expansion we need the result

$$f(z) \equiv \sqrt{1+z^2} = 1 + \frac{z^2}{2} - \frac{z^4}{8} + \frac{z^6}{6} + \frac{5}{128}z^8 + \mathcal{O}(z^{10})\,. \tag{1.1.46}$$

The function $f(z)$ exhibits branch cuts at $z = \pm i$ (see Figure 1.3), thus the expansion of $f(z)$ around $z = 0$ has radius of convergence equal to one: the series converges for $|z| < 1$ and diverges for $|z| > 1$. Table 1 shows $f(z)$ evaluated for $z = 0.9, 1.2$, and 1.5. The various approximations to the full series are shown.

For our expansion of (1.1.45), convergence for $|z| < 1$ implies convergence when

$$\frac{|\lambda||V|}{\frac{1}{2}|E_1^{(0)} - E_2^{(0)}|} < 1 \implies |\lambda V| < \tfrac{1}{2}|E_1^{(0)} - E_2^{(0)}|\,. \tag{1.1.47}$$

For $|\lambda V| > \frac{1}{2}|E_1^{(0)} - E_2^{(0)}|$ the perturbation series does not converge. We learn that for convergence the perturbation must be small compared with *energy differences* in $H^{(0)}$. It is not sufficient that the magnitude of the matrix elements of $\lambda\delta H$ be small compared to those in $H^{(0)}$, energy differences matter. This result leads us to expect complications when energy differences go to zero and $H^{(0)}$ has degeneracies.

z	0.9	1.2	1.5
$f(z)$	1.34536	1.56205	1.80278
$f_8(z)$	1.33939	1.47946	1.20297
$f_{14}(z)$	1.33939	1.67280	4.82288
$f_{20}(z)$	1.34490	1.36568	-18.4895
$f_{30}(z)$	1.34545	2.23047	641.772

Table 1.1: $f(z) \equiv \sqrt{1+z^2} = \sum_i c_i z^i$ and $f_n(z) = \sum_{i=0}^{n} c_i z^i$.

1.1.2 Example: Anharmonic oscillator

Consider the simple harmonic oscillator

$$H^{(0)} = \frac{\hat{p}^2}{2m} + \tfrac{1}{2} m\omega^2 \hat{x}^2 \,. \tag{1.1.48}$$

We want to explore the effect of a perturbation proportional to $\sim \hat{x}^4$. This has the effect of changing the original quadratic potential for a more complicated potential that includes a quartic term. To do analysis in a clear way, we must consider units. Using the constants $\hbar, m, \omega$ of the harmonic oscillator a length scale d can be uniquely build:

$$d^2 = \frac{\hbar}{m\omega} \,. \tag{1.1.49}$$

The unit-free coordinate $\hat{x}/d$ then has a simple expression in terms of creation and annihilation operators:

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a} + \hat{a}^\dagger) = d\,\tfrac{1}{\sqrt{2}}(\hat{a} + \hat{a}^\dagger) \quad \rightarrow \quad \frac{\hat{x}}{d} \;=\; \tfrac{1}{\sqrt{2}}(\hat{a} + \hat{a}^\dagger) \,. \tag{1.1.50}$$

It follows that an $\hat{x}^4$ perturbation with units of energy takes the form

$$\delta H \;=\; \hbar\omega\, \frac{\hat{x}^4}{d^4} \;=\; \frac{m^2\omega^3}{\hbar}\hat{x}^4 \;=\; \tfrac{1}{4}\,\hbar\omega(\hat{a} + \hat{a}^\dagger)^4 \,. \tag{1.1.51}$$

Using the unit-free parameter λ, the perturbed Hamiltonian will therefore be

$$\boxed{H(\lambda) \;=\; H^{(0)} + \lambda\, \frac{m^2\omega^3}{\hbar}\hat{x}^4 \;=\; H^{(0)} + \lambda\, \tfrac{1}{4}\,\hbar\omega(\hat{a} + \hat{a}^\dagger)^4 \,.} \tag{1.1.52}$$

We will identify the states $|k^{(0)}\rangle$ of $H^{(0)}$ with the number eigenstates $|k\rangle$, $k = 0, 1, \ldots$, of the harmonic oscillator. Recall that

$$E_k^{(0)} = \hbar\omega(k + \tfrac{1}{2}) \,, \quad |k\rangle = \frac{(\hat{a}^\dagger)^k}{\sqrt{k!}}|0\rangle \,. \tag{1.1.53}$$

The Hamiltonian $H(\lambda)$ defines an anharmonic oscillator. In a classical anharmonic oscillator the frequency of oscillation depends on the amplitude of oscillation. In the quantum harmonic oscillator all levels are equally spaced. The frequencies associated with transitions between various levels are therefore integer multiples (*i.e.* harmonics) of the basic frequency associated to a transition between the first excited state and the ground state. In the quantum anharmonic oscillator the spacing between the energy levels is not uniform.

First the simplest question: What is the first-order correction $E_0^{(1)}$ to the energy of the ground state? For this, following (1.1.21) we simply calculate the expectation value of the perturbation on the ground state:

$$E_0^{(1)} \;=\; \langle 0|\tfrac{1}{4}\,\hbar\omega(\hat a+\hat a^\dagger)^4|0\rangle \;=\; \tfrac{1}{4}\,\hbar\omega\langle 0|(\hat a+\hat a^\dagger)^4|0\rangle = \tfrac{3}{4}\,\hbar\omega\,, \tag{1.1.54}$$

where we used

$$\langle 0|(\hat a+\hat a^\dagger)^4|0\rangle = 3\,, \tag{1.1.55}$$

as you should verify. It follows that the corrected energy is

$$E_0(\lambda) = E_0^{(0)} + \lambda E_0^{(1)} + \mathcal{O}(\lambda^2) \;= \tfrac{1}{2}\hbar\omega + \lambda\tfrac{3}{4}\hbar\omega + \mathcal{O}(\lambda^2) \;=\; \tfrac{1}{2}\hbar\omega\left(1+\tfrac{3}{2}\lambda+\mathcal{O}(\lambda^2)\right) \tag{1.1.56}$$

We note that the energy of the ground state increases with $\lambda > 0$. This is reasonable as the quartic term in the modified potential squeezes the ground state. How about second order correction to the ground state energy? For this we use (1.1.36) taking $n = 0$:

$$E_0^{(2)} = -\sum_{k\neq 0}\frac{|\delta H_{k0}|^2}{E_k^{(0)}-E_0^{(0)}}\,. \tag{1.1.57}$$

The sum is over all $k \geq 1$ such that δH_{k0} is non-vanishing. Here

$$\delta H_{k0} \;=\; \tfrac{1}{4}\hbar\omega\,\langle k|(\hat a+\hat a^\dagger)^4|0\rangle\,. \tag{1.1.58}$$

We consider $(\hat a+\hat a^\dagger)^4|0\rangle$ which corresponds, up to constants to acting on the ground state wavefunction φ_0 with x^4. This should give an even wavefunction. So $(\hat a+\hat a^\dagger)^4|0\rangle$ must be a superposition of $|0\rangle, |2\rangle$, and $|4\rangle$. We cannot get states with higher number because there are at most four creation operators acting on the vacuum. A short calculation (do it!) confirms that

$$(\hat a+\hat a^\dagger)^4|0\rangle \;=\; 3|0\rangle + 6\sqrt{2}\,|2\rangle + \sqrt{4!}\,|4\rangle\,. \tag{1.1.59}$$

This immediately gives

$$\delta H_{00} = \tfrac{3}{4}\,\hbar\omega\,, \quad \delta H_{20} = \tfrac{3\sqrt{2}}{2}\,\hbar\omega\,, \quad \delta H_{40} = \tfrac{\sqrt{6}}{2}\,\hbar\omega\,, \tag{1.1.60}$$

the first of which we had already determined and is not needed for the second order computation. Back in (1.1.57) we have

$$E_0^{(2)} = -\frac{|\delta H_{20}|^2}{2\hbar\omega} - \frac{|\delta H_{40}|^2}{4\hbar\omega} \;=\; -\frac{(\hbar\omega)^2}{2\hbar\omega}\frac{9}{2} - \frac{(\hbar\omega)^2}{4\hbar\omega}\frac{3}{2} = -\left(\tfrac{9}{4}+\tfrac{3}{8}\right)\hbar\omega \;=\; -\tfrac{21}{8}\hbar\omega\,. \tag{1.1.61}$$

Therefor the corrected ground state energy to quadratic order is

$$\boxed{E_0^{(0)} + \lambda E_0^{(1)} + \lambda^2 E_0^{(2)} \;=\; \tfrac{1}{2}\hbar\omega\,\left(1 + \tfrac{3}{2}\lambda - \tfrac{21}{4}\lambda^2\right)\,.} \tag{1.1.62}$$

The computation can be carried to higher order, as first done by Bender and Wu (Phys. Rev.**184** (1969)1231). They find that[1]

$$E_0(\lambda) = \tfrac{1}{2}\hbar\omega\left(1 + \tfrac{3}{2}\lambda - \tfrac{21}{4}\lambda^2 + \tfrac{333}{8}\,\lambda^3 - \tfrac{30885}{64}\,\lambda^4 + \tfrac{916731}{128}\,\lambda^5 - \tfrac{65518401}{512}\lambda^6 + \mathcal{O}(\lambda^7)\right) \tag{1.1.63}$$

As it turns out the coefficients keep growing and the series does not converge for any nonzero λ; the radius of convergence is actually zero! This does not mean the series is not useful. It is an asymptotic expansion. This means that for a given small value of λ the magnitude of successive terms generally decrease until, at some point, they start growing again. A good approximation to the desired answer is obtained by including only the part of the sum where the terms are decreasing.

Exercise 3. Calculate the first order correction $E_n^{(1)}$ to the energy for the state $|n\rangle$ of number n. Exhibit the anharmonicity of the oscillator by using this result to find, to first order in λ, the energy separation $\Delta E_n(\lambda) = E_n(\lambda) - E_{n-1}(\lambda)$ between levels.

Let us now find the first order correction to the ground-state wavefunction. Using (1.1.34) with $n = 0$ we have

$$|0^{(1)}\rangle = -\sum_{k\neq 0} \frac{\delta H_{k0}}{E_k^{(0)} - E_0^{(0)}}\,|k\rangle\,. \tag{1.1.64}$$

We then find

$$\begin{aligned} |0^{(1)}\rangle \;&=\; -\frac{\delta H_{20}}{2\hbar\omega}|2\rangle - \frac{\delta H_{40}}{4\hbar\omega}|4\rangle \;=\; -\tfrac{3}{4}\sqrt{2}|2\rangle - \tfrac{1}{16}\sqrt{4!}|4\rangle \\ &=\; -\tfrac{3}{4}\,\hat{a}^\dagger\hat{a}^\dagger|0\rangle - \tfrac{1}{16}\,\hat{a}^\dagger\hat{a}^\dagger\hat{a}^\dagger\hat{a}^\dagger|0\rangle\,. \end{aligned} \tag{1.1.65}$$

This means that to first order the ground state of the perturbed oscillator is

$$\boxed{|0\rangle_\lambda \;=\; |0\rangle - \lambda\left(\tfrac{3}{4}\,\hat{a}^\dagger\hat{a}^\dagger|0\rangle + \tfrac{1}{16}\,\hat{a}^\dagger\hat{a}^\dagger\hat{a}^\dagger\hat{a}^\dagger|0\rangle\right) + \mathcal{O}(\lambda^2)\,.} \tag{1.1.66}$$

1.2 Degenerate perturbation theory

If the spectrum of $H^{(0)}$ has degenerate states, as shown in Figure 1.1, tracking the evolution of those states as λ becomes nonzero presents new challenges. We first show that naive extrapolation of our results for a non-degenerate state do not work. We will also be able to appreciate the basic difficulty.

[1]Bender and Wu's results, in eqns. (2.12) of their paper must all be multiplied by a factor of 2, as they take $A_0 = 1/2$.

1.2.1 Degenerate toy model

Consider an example with two-by-two matrices. The unperturbed matrix $H^{(0)}$ will be set equal to the identity matrix:

$$H^{(0)} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} . \tag{1.2.1}$$

We have a degeneracy here as the two eigenvalues are identical (and equal to one). The perturbation matrix δH is chosen to be off diagonal:

$$\delta H = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} . \tag{1.2.2}$$

We then have

$$H(\lambda) = H^{(0)} + \lambda \delta H = \begin{pmatrix} 1 & \lambda \\ \lambda & 1 \end{pmatrix} . \tag{1.2.3}$$

Using labels $n = 1, 2$ the unperturbed eigenstates can be taken to be

$$|1^{(0)}\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} , \quad |2^{(0)}\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} , \qquad E_1^{(0)} = E_2^{(0)} = 1 , \tag{1.2.4}$$

with the corresponding eigenvalues indicated as well. To first order in λ, the eigenvalues predicted from non-degenerate perturbation theory (1.1.37) are $E_n(\lambda) = E_n^{(0)} + \lambda \delta H_{nn}$. This gives

$$\begin{aligned} E_1(\lambda) &= E_1^{(0)} + \lambda \delta H_{11} = 1 + \lambda \cdot 0 = 1 \ ? \\ E_1(\lambda) &= E_2^{(0)} + \lambda \delta H_{22} = 1 + \lambda \cdot 0 = 1 \ ? \end{aligned} \tag{1.2.5}$$

The eigenvalues are unperturbed to first order in λ since the matrix δH is off-diagonal. These answers, however, are wrong. We can compute the exact eigenvalues of $H(\lambda)$ and they are $1 \pm \lambda$. There is also a problem with the state corrections. Equation (1.1.37) states that

$$|n\rangle_\lambda = |n^{(0)}\rangle - \lambda \sum_{k \neq n} \frac{\delta H_{kn}}{E_k^{(0)} - E_n^{(0)}} |k^{(0)}\rangle . \tag{1.2.6}$$

but this time, with $E_1^{(0)} = E_2^{(0)}$ the denominator is zero, and the δH matrix element is also zero, giving us an ambiguous result.

So what can we do? A direct calculation shows that

$$H(\lambda) \text{ has eigenvectors} \quad \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \qquad \text{with eigenvalue } = 1 + \lambda , \tag{1.2.7}$$

$$\text{and} \quad \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \qquad \text{with eigenvalue } = 1 - \lambda . \tag{1.2.8}$$

You may think the eigenvectors jump from those of $H^{(0)}$ indicated in (1.2.4) to those of $H(\lambda)$ as soon as λ becomes nonzero. Such discontinuity is totally against the spirit of

perturbation theory. Happily, this is not really true. The eigenvectors of $H^{(0)}$ are in fact *ambiguous*, precisely due to the degeneracy. The eigenvectors of $H^{(0)}$ are actually the *span* of the two vectors listed in (1.2.4). The perturbation selected a particular combination of these eigenvectors. This particular combination is the one that we should use even for $\lambda = 0$. The lesson is that to get states that vary continuously as λ is turned on we must choose the basis in the degenerate subspace of $H^{(0)}$ carefully. We will call that carefully selected basis the "good" basis.

1.2.2 Systematic Analysis

Again, we are looking at the perturbed Hamiltonian

$$H(\lambda) = H^{(0)} + \lambda \delta H \,, \tag{1.2.9}$$

where $H^{(0)}$ has known eigenvectors and eigenvalues. We will focus this time on a degenerate subspace of eigenvectors of dimension $N > 1$, that is, a space with N linearly independent eigenstates of the same energy. In the basis of eigenstates, $H^{(0)}$ is a diagonal matrix that contains a string of $N > 1$ identical entries:

$$H^{(0)} = \text{diag}\,\{\, E_1^{(0)}, E_2^{(0)}, \ldots, \underbrace{E_n^{(0)}, \ldots, E_n^{(0)}}_{N}, \ \ldots \} \,. \tag{1.2.10}$$

In the degenerate subspace we choose a collection of N orthonormal eigenstates

$$|n^{(0)}; 1\rangle \,, |n^{(0)}; 2\rangle, \ \ldots, \ |n^{(0)}; N\rangle \,. \tag{1.2.11}$$

Accordingly, we have

$$\langle n^{(0)}; p \, | n^{(0)}; l \rangle \ = \ \delta_{p,l} \,, \tag{1.2.12}$$

$$H^{(0)} | n^{(0)}; k \rangle \ = \ E_n^{(0)} | n^{(0)}; k \rangle \,. \tag{1.2.13}$$

This set of vectors span a degenerate subspace of dimension N that we will call $\mathbb{V}_N$

$$\mathbb{V}_N \ \equiv \ \text{span}\{ |n^{(0)}; k\rangle, k = 1, \ldots N \} \,. \tag{1.2.14}$$

The total state space of the theory, denoted by $\mathcal{H}$ is written as a direct sum:

$$\mathcal{H} = \mathbb{V}_N \oplus \hat{V} \,, \tag{1.2.15}$$

where $\hat{V}$ is spanned by those eigenstates of $H^{(0)}$ that are not in $\mathbb{V}_N$. We denote by $|p^{(0)}\rangle$ with $p \in \mathbb{Z}$ a basis for $\hat{V}$. That basis may include both degenerate and non degenerate states. Together with the states in $\mathbb{V}_N$ we have an orthonormal basis for the whole state space:

$$\langle p^{(0)} | q^{(0)} \rangle \ = \ \delta_{pq} \,, \qquad \langle p^{(0)} | n^{(0)}; k \rangle \ = \ 0 \,. \tag{1.2.16}$$

Our notation distinguishes the states in $\mathbb{V}_N$ from those in $\hat{V}$ because the former have two labels and the latter have only one.

We now consider the evolution of the degenerate eigenstates as we turn on the perturbation. Again we assume that the states vary continuously in λ and thus write:

$$\begin{aligned} |n^{(0)};k\rangle \to \quad |n;k\rangle_\lambda &= |n^{(0)};k\rangle + \lambda|n^{(1)};k\rangle + \lambda^2|n^{(2)};k\rangle + \mathcal{O}(\lambda^3)\,, \\ E_n^{(0)} \to \quad E_{n,k}(\lambda) &= E_n^{(0)} + \lambda\, E_{n,k}^{(1)} + \lambda^2\, E_{n,k}^{(2)} + \mathcal{O}(\lambda^3)\,. \end{aligned} \tag{1.2.17}$$

These equations hold for $k = 1, \ldots, N$. Note that for each value of k the energy corrections might be different and that's why the energy corrections carry the label k. Our goal is to find the state corrections $|n^{(p)};k\rangle$ and the energy corrections $E_{n,k}^{(p)}$ for $p \geq 1$ and for each k. As before we demand that $|n^{(p)};k\rangle$ for $p \geq 1$ has no component along $|n^{(0)};k\rangle$, i.e.

$$\langle n^{(0)};k|n^{(p)};k\rangle = 0 \qquad \text{for} \;\; p \geq 1 \tag{1.2.18}$$

Note, however, that $|n^{(p)};k\rangle$ may have components along $|n^{(0)};\ell\rangle$ with $\ell \neq k$. So $|n^{(0)};k\rangle$ may and in fact will have a component in $\mathbb{V}_N$.

The perturbed eigenstates must satisfy

$$H(\lambda)\,|n;k\rangle_\lambda \;=\; E_{n,k}(\lambda)\,|n;k\rangle_\lambda\,, \tag{1.2.19}$$

and substituting the perturbative expansions above we obtain equations completely analogous to the ones in Eq.(1.1.13)

$$\lambda^0: \qquad (H^0 - E_n^{(0)})\,|n^{(0)};k\rangle \;=\; 0\,, \tag{1.2.20}$$

$$\lambda^1: \qquad (H^0 - E_n^{(0)})\,|n^{(1)};k\rangle \;=\; (E_{n,k}^{(1)} - \delta H)|n^{(0)};k\rangle\,, \tag{1.2.21}$$

$$\lambda^2: \qquad (H^0 - E_n^{(0)})\,|n^{(2)};k\rangle \;=\; (E_{n,k}^{(1)} - \delta H)|n^{(1)};k\rangle \;+\; E_{n,k}^{(2)}\,|n^{(0)};k\rangle\,, \tag{1.2.22}$$

$$\vdots \qquad\qquad \vdots \qquad\qquad \vdots$$

In the following we will discuss a solution to first order for the case in which the degeneracy in $\mathbb{V}_N$ is completely broken to first order in perturbation theory; that is, the first order corrections to the energies split the N states completely. Our solution will proceed in three steps:

1. Hit the $\mathcal{O}(\lambda)$ equation with $\langle n^{(0)};\ell|$ to learn that δH must be diagonal in the chosen basis for $\mathbb{V}_N$ and to determine the first-order energy shifts.

2. Use the $\mathcal{O}(\lambda)$ equation to calculate the components of $|n^{(1)};k\rangle$ in $\hat{V}$.

3. Hit the $\mathcal{O}(\lambda^2)$ equation with $\langle n^{(0)};\ell|$ to determine the second order energy correction $E_{n,k}^{(2)}$ and the component of $|n^{(1)};k\rangle$ in $\mathbb{V}_N$.

Step 1. Recalling that $\langle n^{(0)};\ell|(H^{(0)}-E_n^{(0)})=0$, as we hit the $\mathcal{O}(\lambda)$ equation with $\langle n^{(0)};\ell|$ the left-hand side vanishes and we find

$$\langle n^{(0)};\ell|(E^{(1)}_{n,k}-\delta H)|n^{(0)};k\rangle = 0\,. \tag{1.2.23}$$

Since the basis states in $\mathbb{V}_N$ are orthonormal, this implies that

$$\langle n^{(0)};\ell|\,\delta H\,|n^{(0)};k\rangle \;=\; E^{(1)}_{n,k}\,\delta_{\ell,k}\,. \tag{1.2.24}$$

This equation holds for all $k,\ell=1,\ldots,N$. Remarkably, this equation is telling us that the basis $|n^{(0)};k\rangle$ *must be chosen* to make the matrix δH diagonal in the subspace $\mathbb{V}_N$! This is required in order to get the perturbation theory going. Setting ℓ equal to k we read the values of the first order energy shifts

$$E^{(1)}_{n,k} \;=\; \langle n^{(0)};k|\delta H|n^{(0)};k\rangle \;=\; \delta H_{nk,nk}\,, \tag{1.2.25}$$

where the last equality is a definition. The energies to first order are then

$$\boxed{\;E_{n,k}(\lambda) \;=\; E^{(0)}_n+\lambda\,\delta H_{nk,nk}\,.\;} \tag{1.2.26}$$

A few remarks:

1. The above result for the first order energy shifts is true *always*, even if the degeneracy is not lifted. The degeneracy is lifted when

$$E^{(1)}_{n,k} \;\neq\; E^{(1)}_{n,\ell}\,,\quad \text{whenever}\quad k\neq\ell\,, \tag{1.2.27}$$

for all values of $k,\ell=1,\ldots,N$. This assumption will be used in the later steps. If the degeneracy is lifted, the basis states $|n^{(0)};k\rangle$ that make δH diagonal in $\mathbb{V}_N$ are called "good states" or a "good basis". This means that they are the basis states in $\mathbb{V}_N$ that get deformed continuously as λ becomes non-zero. If the degeneracy is not lifted to first order the determination of the good basis has to be attempted to second order.

2. The perturbation δH is diagonalized in the subspace $\mathbb{V}_N$. The perturbation δH is *not* diagonal on the whole space $\mathcal{H}$, only within the block representing $\mathbb{V}_N$ is δH a diagonal matrix. Alternatively we can see this via the action of δH on the basis states. Introducing a resolution of the identity, we have

$$\begin{aligned}\delta H|n^{(0)};\ell\rangle \;&=\; \sum_q |n^{(0)};q\rangle\,\langle n^{(0)};q|\delta H|n^{(0)};\ell\rangle+\sum_p |p^{(0)}\rangle\,\langle p^{(0)}|\delta H|n^{(0)};\ell\rangle\\ &=\; \sum_q E^{(1)}_{n,\ell}\delta_{\ell,q}|n^{(0)};q\rangle+\sum_p |p^{(0)}\rangle\,\langle p^{(0)}|\delta H|n^{(0)};\ell\rangle\\ &=\; E^{(1)}_{n,\ell}|n^{(0)};\ell\rangle+\sum_p |p^{(0)}\rangle\,\langle p^{(0)}|\delta H|n^{(0)};\ell\rangle\,.\end{aligned} \tag{1.2.28}$$

This shows that the states $|n^{(0)};\ell\rangle$ are *almost* δH eigenstates with eigenvalues equal to the first order energy corrections. The failure is an extra state along $\hat{V}$.

3. We can sometimes assess without computation that a certain basis in $\mathbb{V}_N$ makes δH diagonal. Here is a rule: *the matrix δH is diagonal for a choice of basis in $\mathbb{V}_N$ if there is a Hermitian operator K that commutes with δH for which the chosen basis vectors are K eigenstates with different eigenvalues.* This is quickly established. Consider two different basis states in $\mathbb{V}_N$: $|n^{(0)};p\rangle$ and $|n^{(0)};q\rangle$, with $p\neq q$. Assume these have K eigenvalues λ_p and λ_q, respectively. Since $[\delta H,K]=0$:

$$0 \;=\; \langle n^{(0)};p|[\delta H,K]|n^{(0)};q\rangle \;=\; (\lambda_q-\lambda_p)\langle n^{(0)};p|\,\delta H\,|n^{(0)};q\rangle\,. \tag{1.2.29}$$

Since the eigenvalues λ_p and λ_q are presumed to be different, the non-diagonal matrix elements of δH vanish.

Step 2. The $\mathcal{O}(\lambda)$ equation cannot determine the component of $|n^{(1)};k\rangle$ along $\mathbb{V}_N$. As we will see later, such piece is required by consistency and gets determined from the $\mathcal{O}(\lambda^2)$ equation. We now determine the piece of $|n^{(1)};k\rangle$ along $\hat{V}$. For this we hit the $\mathcal{O}(\lambda)$ equation with $\langle p^{(0)}|$ to find

$$\langle p^{(0)}|(H^{(0)}-E_n^{(0)})|n^{(1)};k\rangle \;=\; \langle p^{(0)}|\,(\;\overbrace{E_{n,k}^{(1)}}^{|p^{(0)}\rangle\perp\mathbb{V}_N}-\delta H\,)\,|n^{(0)};k\rangle \tag{1.2.30}$$

and we get

$$(E_p^{(0)}-E_n^{(0)})\langle p^{(0)}|n^{(1)};k\rangle \;=\; -\delta H_{p,nk}\,, \tag{1.2.31}$$

where we introduced the matrix element $\delta H_{p,nk}\equiv\langle p^{(0)}|\,\delta H\,|n^{(0)};k\rangle$. Our equation above means that the piece of $|n^{(1)};k\rangle$ in $\hat{V}$ is now determined:

$$|n^{(1)};k\rangle = \;-\sum_p \frac{\delta H_{p,nk}}{E_p^{(0)}-E_n^{(0)}}|p^{(0)}\rangle + |n^{(1)};k\rangle\Big|_{\mathbb{V}_N}\,, \tag{1.2.32}$$

where we included explicitly the still undetermined piece of $|n^{(1)};k\rangle$ along $\mathbb{V}_N$.

Step 3. We now hit we hit the $\mathcal{O}(\lambda^2)$ equation with $\langle n^{(0)};\ell|$. The left-hand side vanishes and using the above expression for $|n^{(1)};k\rangle$ we find

$$\begin{aligned} 0 \;=\;& -\langle n^{(0)};\ell|(E_{n,k}^{(1)}-\delta H)\sum_p|p^{(0)}\rangle\,\frac{\delta H_{p,nk}}{E_p^{(0)}-E_n^{(0)}} \\ & +\langle n^{(0)};\ell|(E_{n,k}^{(1)}-\delta H)|n^{(1)};k\rangle\Big|_{\mathbb{V}_N}+E_{n,k}^{(2)}\delta_{k,\ell}\,. \end{aligned} \tag{1.2.33}$$

In the first term on the right-hand side, the part proportional to $E_{n,k}^{(1)}$ vanishes by orthonormality. On the second line, the term including δH can be simplified because δH is diagonal within $\mathbb{V}_N$. Recalling (1.2.28) we have

$$\langle n^{(0)};\ell|\delta H \;=\; E_{n,\ell}^{(1)}\,\langle n^{(0)};\ell|\;+\sum_p\langle n^{(0)};\ell|\delta H|p^{(0)}\rangle\,\langle p^{(0)}|\,. \tag{1.2.34}$$

The piece in $\hat{V}$ vector drops out for our case of interest:

$$\langle n^{(0)};\ell|\delta H|n^{(1)};k\rangle\Big|_{\mathbb{V}_N} \;=\; E^{(1)}_{n,\ell}\,\langle n^{(0)};\ell|n^{(1)};k\rangle\Big|_{\mathbb{V}_N}\,. \tag{1.2.35}$$

Back into equation (1.2.33) we now get

$$\sum_p \frac{\delta H_{n\ell,p}\delta H_{p,nk}}{E^{(0)}_p - E^{(0)}_n} + \Big(E^{(1)}_{n,k} - E^{(1)}_{n,\ell}\Big)\,\langle n^{(0)};\ell|n^{(1)};k\rangle\Big|_{\mathbb{V}_N} + E^{(2)}_{n,k}\delta_{k,\ell} = 0\,. \tag{1.2.36}$$

Setting $\ell = k$ we can determine the second correction to the energies:

$$E^{(2)}_{n,k} \;=\; -\sum_p \frac{|\delta H_{p,nk}|^2}{E^{(0)}_p - E^{(0)}_n}\,. \tag{1.2.37}$$

For $k \neq \ell$ we get

$$\sum_p \frac{\delta H_{n\ell,p}\delta H_{p,nk}}{E^{(0)}_p - E^{(0)}_n} + \Big(E^{(1)}_{n,k} - E^{(1)}_{n,\ell}\Big)\,\langle n^{(0)};\ell|n^{(1)};k\rangle\Big|_{\mathbb{V}_N} = 0\,. \tag{1.2.38}$$

Had we not included the piece of $|n^{(1)};k\rangle$ along the degenerate subspace we would have had an inconsistency, since there is no reason why the first term on the left-hand side must be zero. Now the above equation just fixes the components of $|n^{(1)};k\rangle$ in the degenerate subspace *as long as* $E^{(1)}_{n,k} \neq E^{(1)}_{n,\ell}$:

$$\langle n^{(0)};\ell|n^{(1)};k\rangle\Big|_{\mathbb{V}_N} \;=\; -\frac{1}{E^{(1)}_{n,k} - E^{(1)}_{n,\ell}}\sum_p \frac{\delta H_{n\ell,p}\delta H_{p,nk}}{E^{(0)}_p - E^{(0)}_n}\;, \qquad k \neq \ell. \tag{1.2.39}$$

We thus have

$$|n^{(1)};k\rangle\Big|_{\mathbb{V}_N} = \; -\sum_{\ell\neq k} |n^{(0)};\ell\rangle\,\frac{1}{E^{(1)}_{n,k} - E^{(1)}_{n,\ell}}\,\sum_p \frac{\delta H_{n\ell,p}\delta H_{p,nk}}{E^{(0)}_p - E^{(0)}_n}\,. \tag{1.2.40}$$

It may seem that this extra piece, found by using the $\mathcal{O}(\lambda^2)$ equation, is higher order than it should in the perturbation: its numerator contains two powers of δH. But this expression also has a curious energy denominator, $E^{(1)}_{n,k} - E^{(1)}_{n,\ell}$, in which each term has a power of δH. All in all, the correction to the state is properly first order in δH.

Summarizing our result we have

Degenerate perturbation theory with degeneracies lifted at $\mathcal{O}(\lambda)$:

$$|n;k\rangle_\lambda \;=\; |n^{(0)};k\rangle - \lambda\Big(\sum_p \frac{\delta H_{p,nk}}{E^{(0)}_p - E^{(0)}_n}|p^{(0)}\rangle + \sum_{\ell\neq k}\frac{|n^{(0)};\ell\rangle}{E^{(1)}_{n,k} - E^{(1)}_{n,\ell}}\,\sum_p \frac{\delta H_{n\ell,p}\delta H_{p,nk}}{E^{(0)}_p - E^{(0)}_n}\Big) + \mathcal{O}(\lambda^2)$$

$$E_{n,k}(\lambda) \;=\; E^{(0)}_n \;+\lambda\,\delta H_{nk,nk} \;-\;\lambda^2\sum_p \frac{\delta H_{nk,p}\,\delta H_{p,nk}}{E^{(0)}_p - E^{(0)}_n} + \mathcal{O}(\lambda^3)\,, \qquad E^{(1)}_{n,k} \;=\; \delta H_{nk,nk}\,. \tag{1.2.41}$$

1.2.3 Degeneracy lifted at second order

We now investigate the case when the degeneracy is completely unbroken to first order. The situation and the setup is similar to the one we just considered: we have a degenerate subspace $\mathbb{V}_N$ of dimension N and the rest of the space is called $\hat{V}$. This time, however, we will assume that the degeneracy of $H^{(0)}$ is not broken to first order in the perturbation δH. Concretely, this means that on the $\mathbb{V}_N$ basis $|n^{(0)}; k\rangle$ with $k = 1, \ldots, N$, we have

$$\langle n^{(0)}; \ell|\, \delta H\, |n^{(0)}; k\rangle \;=\; E_n^{(1)}\, \delta_{\ell,k}\,. \tag{1.2.42}$$

The first order energy correction is the same, and equal to $E_n^{(1)}$, for all basis states in $\mathbb{V}_N$. You should compare with (1.2.24), where the energy had an extra subscript to distinguish its various possible values.

Because the degeneracy is not broken to first order we do not know at this point what is the good basis in $\mathbb{V}_N$. We will consider here the case when the degeneracy is completely lifted to second order. We express our ignorance about good basis vectors by stating that we are searching for the right linear combinations:

$$|\psi^{(0)}\rangle = \sum_{k=1}^{N} |n^{(0)}; k\rangle\, a_k^{(0)}\,. \tag{1.2.43}$$

For some values of the constants $a_k^{(0)}$ with $k = 1, \ldots, N$ the state $|\psi^{(0)}\rangle$ will be good. We can think of $a^{(0)}$ as the column vector representation of $|\psi^{(0)}\rangle$ in $\mathbb{V}_N$. We have written just one state, $|\psi^{(0)}\rangle$, even though we are expecting to find N good states to span the degenerate subspace. We therefore adjust the notation to reflect this. We introduce a new index $I = 1, \ldots, N$ and write

$$|\psi_I^{(0)}\rangle = \sum_{k=1}^{N} |n^{(0)}; k\rangle\, a_{Ik}^{(0)}\,, \quad I = 1, \ldots, N\,. \tag{1.2.44}$$

The index I now labels the different good states and their different vector representations $a_I^{(0)}$. Our most immediate goal is to find those vectors $a_I^{(0)}$ and thus the good basis. To do so we will have to consider second order energy corrections. The states $|\psi_I^{(0)}\rangle$ form an orthonormal basis in $\mathbb{V}_N$ if the coefficients $a_I^{(0)}$ satisfy

$$\langle\psi_J^{(0)}|\psi_I^{(0)}\rangle = \delta_{IJ} \quad\to\quad \sum_k (a_{Jk}^{(0)})^*\, a_{Ik}^{(0)} \;=\; \delta_{IJ}\,. \tag{1.2.45}$$

We set up the perturbation theory as usual

$$\begin{aligned} |\psi_I\rangle_\lambda \;&=\; |\psi_I^{(0)}\rangle + \lambda|\psi_I^{(1)}\rangle + \lambda^2|\psi_I^{(2)}\rangle + \ldots\,, \\ E_{nI}(\lambda) \;&=\; E_n^{(0)} \;+\lambda\, E_n^{(1)} \;+\lambda^2\, E_{nI}^{(2)} \;+\lambda^3\, E_{nI}^{(3)} + \ldots\,. \end{aligned} \tag{1.2.46}$$

Note that in the energy expansion we have accounted for the degeneracy to zeroth and first order: the index I first appears in the second-order corrections to the energy. Using the Schrödinger equation

$$H(\lambda)|\psi_I\rangle_\lambda \;=\; E_{nI}(\lambda)|\psi_I\rangle_\lambda\,, \tag{1.2.47}$$

gives the by now familiar equations, of which we list the first four:

$$\begin{aligned}
\lambda^0\,: \qquad & (H^{(0)}-E_n^{(0)})\,|\psi_I^{(0)}\rangle \;=\; 0\,,\\
\lambda^1\,: \qquad & (H^{(0)}-E_n^{(0)})\,|\psi_I^{(1)}\rangle \;=\; (E_n^{(1)}-\delta H)|\psi_I^{(0)}\rangle\,,\\
\lambda^2\,: \qquad & (H^{(0)}-E_n^{(0)})\,|\psi_I^{(2)}\rangle \;=\; (E_n^{(1)}-\delta H)|\psi_I^{(1)}\rangle \,+\, E_{nI}^{(2)}\,|\psi_I^{(0)}\rangle\,,\\
\lambda^3\,: \qquad & (H^{(0)}-E_n^{(0)})\,|\psi_I^{(3)}\rangle \;=\; (E_n^{(1)}-\delta H)|\psi_I^{(2)}\rangle + \,E_{nI}^{(2)}\,|\psi_I^{(1)}\rangle \,+\, E_{nI}^{(3)}\,|\psi_I^{(0)}\rangle\,.
\end{aligned} \tag{1.2.48}$$

The zero-th order equation is trivially satisfied. For the order λ equation the overlap with $\langle n^{(0)};\ell|$ works out automatically, without giving any new information. Indeed, the left-hand side vanishes and we thus get

$$0 \;=\; \langle n^{(0)};\ell|(E_n^{(1)}-\delta H)|\psi_I^{(0)}\rangle\,. \tag{1.2.49}$$

Since $\langle n^{(0)};\ell|$ is a δH eigenstate with eigenvalue $E_n^{(1)}$, up to a vector in $\hat{V}$ (see (1.2.34)), the above right-hand side vanishes. Acting on the order λ equation with $\langle p^{(0)}|$ gives useful information:

$$(E_p^{(0)}-E_n^{(0)})\langle p^{(0)}|\psi_I^{(1)}\rangle \;=\; \langle p^{(0)}|(E_n^{(1)}-\delta H)|\psi_I^{(0)}\rangle \;=\; -\langle p^{(0)}|\delta H|\psi_I^{(0)}\rangle\,, \tag{1.2.50}$$

using the orthogonality of $\hat{V}$ and $\mathbb{V}_N$. Letting

$$\delta H_{pI} \;\equiv\; \langle p^{(0)}|\delta H|\psi_I^{(0)}\rangle\,, \tag{1.2.51}$$

we then have

$$\langle p^{(0)}|\psi_I^{(1)}\rangle = -\frac{\delta H_{pI}}{E_p^{(0)}-E_n^{(0)}}\,. \tag{1.2.52}$$

Since the ket $|\psi_I^{(0)}\rangle$ is still undetermined, it makes sense to write this information about $|\psi_I^{(1)}\rangle$ in terms of the unknown $a_I^{(0)}$ coefficients. We have

$$\delta H_{pI} \;\equiv\; \sum_{k=1}^{N}\langle p^{(0)}|\delta H|n^{(0)};k\rangle a_{Ik}^{(0)} = \sum_{k=1}^{N}\delta H_{p,nk}\,a_{Ik}^{(0)}\,, \tag{1.2.53}$$

Back into (1.2.52) we get

$$\langle p^{(0)}|\psi_I^{(1)}\rangle = -\frac{1}{E_p^{(0)}-E_n^{(0)}}\sum_{k=1}^{N}\delta H_{p,nk}\,a_{Ik}^{(0)}\,. \tag{1.2.54}$$

This gives the piece of $|\psi_I^{(1)}\rangle$ in $\hat{V}$ in terms of the unknown zeroth order eigenstates.

We have now extracted all the information from the order λ equation. We look now at the order λ^2 equation, which contains the second order corrections to the energy and therefore should help us determine the zeroth order good states. We hit that equation with $\langle n^{(0)};\ell|$ and we get

$$0 \;=\; \langle n^{(0)};\ell|(E_n^{(1)}-\delta H)|\psi_I^{(1)}\rangle\Big|_{\hat{V}} + \langle n^{(0)};\ell|(E_n^{(1)}-\delta H)|\psi_I^{(1)}\rangle\Big|_{\mathbb{V}_N} + E_{nI}^{(2)}a_{I\ell}^{(0)}\,. \tag{1.2.55}$$

Happily, the second term, involving the components of $|\psi_I^{(1)}\rangle$ along $\mathbb{V}_N$, vanishes because of the by now familiar property (1.2.28) adapted to this case. The piece with $E_n^{(1)}$ on the first term also vanishes. We are thus left with

$$0 \;=\; -\langle n^{(0)};\ell|\delta H|\psi_I^{(1)}\rangle\Big|_{\hat{V}} + E_{nI}^{(2)}a_{I\ell}^{(0)}\,. \tag{1.2.56}$$

Introducing a resolution of the identity to the immediate right of δH, only the basis states in $\hat{V}$ contribute and we get

$$0 \;=\; -\sum_p \langle n^{(0)};\ell|\delta H|p^{(0)}\rangle\langle p^{(0)}|\psi_I^{(1)}\rangle + E_{nI}^{(2)}a_{I\ell}^{(0)}\,, \tag{1.2.57}$$

where there is no need to copy the $|_{\hat{V}}$ anymore. Using the result in (1.2.54) we now get

$$0 \;=\; \sum_p \delta H_{nl,p}\frac{1}{E_p^{(0)}-E_n^{(0)}}\sum_{k=1}^N \delta H_{p,nk}\,a_{Ik}^{(0)} + \sum_{k=1}^N E_{nI}^{(2)}\delta_{\ell k}a_{Ik}^{(0)} \tag{1.2.58}$$

Reordering sums and multiplying by minus one we get

$$\sum_{k=1}^N\left(-\sum_p \frac{\delta H_{nl,p}\delta H_{p,nk}}{E_p^{(0)}-E_n^{(0)}} \;-\; E_{nI}^{(2)}\delta_{\ell k}\right)a_{Ik}^{(0)} \;=\; 0\,. \tag{1.2.59}$$

To understand better this equation we define the $N\times N$ Hermitian matrix $M^{(2)}$

$$M_{\ell,k}^{(2)} \;\equiv\; -\sum_p \frac{\delta H_{n\ell,p}\,\delta H_{p,nk}}{E_p^{(0)}-E_n^{(0)}}\,. \tag{1.2.60}$$

The equation then becomes

$$\sum_{k=1}^N\Big(M_{\ell,k}^{(2)} \;-\; E_{nI}^{(2)}\delta_{\ell k}\Big)a_{Ik}^{(0)} \;=\; 0\,. \tag{1.2.61}$$

Recalling that the Kronecker delta is the matrix representation of the identity, we have

$$\Big(M^{(2)} - E_{nI}^{(2)}\mathbb{1}\Big)\;a_I^{(0)} \;=\; 0\,. \tag{1.2.62}$$

This is an eigenvalue equation that tells us that the energy corrections $E^{(2)}_{nI}$ are the eigenvalues of $M^{(2)}$ and the vectors $a^{(0)}_I$ are the associated normalized eigenvectors. These determine, via (1.2.44), our orthonormal basis of good zeroth order states. If δH is known, the matrix $M^{(2)}$ is computable and Hermitian and can therefore be diagonalized.

We will leave the computation of the component of $|\psi^{(1)}_I\rangle$ on the degenerate subspace. That can be done if the degeneracy is completely broken to quadratic order (the eigenvalues of $M^{(2)}$ are all different). Still, it takes some effort and one must use the order λ^3 equation. Our results so far are

$$\begin{aligned} |\psi_I\rangle_\lambda &= |\psi^{(0)}_I\rangle + \lambda\Big(\sum_p |p^{(0)}\rangle \frac{\delta H_{pI}}{E^{(0)}_n - E^{(0)}_p} + \sum_{J\neq I} |\psi^{(0)}_J\rangle\, a^{(1)}_{I,J}\Big) + \mathcal{O}(\lambda^2)\,, \\ E_{In}(\lambda) &= E^{(0)}_n + \lambda\, E^{(1)}_n + \lambda^2\, E^{(2)}_{In} + \lambda^3\, E^{(3)}_{In} + \ldots \mathcal{O}(\lambda^3)\,. \end{aligned} \tag{1.2.63}$$

Here the $a^{(1)}_{I,J}$ are still unknown coefficients that determine the component of the first correction to the states along the degenerate subspace. If you followed the discussion, all other symbols in the above equations have been defined and are computable given δH.

The answer for the coefficients $a^{(1)}_{I,J}$ turns out to be

$$a^{(1)}_{I,J} = \frac{1}{E^{(2)}_{nI} - E^{(2)}_{nJ}} \left[\sum_{p,q} \frac{\delta H_{Jp}\, \delta H_{pq}\, \delta H_{qI}}{(E^{(0)}_p - E^{(0)}_n)(E^{(0)}_q - E^{(0)}_n)} - E^{(1)}_n \sum_p \frac{\delta H_{Jp}\, \delta H_{pI}}{\big(E^{(0)}_p - E^{(0)}_n\big)^2} \right]. \tag{1.2.64}$$

The third order corrections to the energy are

$$E^{(3)}_{In} = \sum_{p,q} \frac{\delta H_{Ip}\, \delta H_{pq}\, \delta H_{qI}}{(E^{(0)}_p - E^{(0)}_n)(E^{(0)}_q - E^{(0)}_n)} - E^{(1)}_n \sum_p \frac{|\delta H_{pI}|^2}{\big(E^{(0)}_p - E^{(0)}_n\big)^2}\,. \tag{1.2.65}$$

Chapter 2

Fine Structure

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2.1 Review of hydrogen atom

The hydrogen atom Hamiltonian is by now familiar to you. You have found the bound state spectrum in more than one way and learned about the large degeneracy that exists for all states except the ground state. We will call the hydrogen atom Hamiltonian $H^{(0)}$ and it is given by

$$H^{(0)} = \frac{\mathbf{p}^2}{2m} - \frac{e^2}{r}\,. \tag{2.1.1}$$

We take this to be the "known" Hamiltonian, meaning that we know its spectrum. This Hamiltonian is supplemented with corrections that can be studied in perturbation theory. That study is the subject of this chapter. We begin, however, with some review and comments.

The mass m in $H^{(0)}$ is the reduced mass of the electron and proton, which we can accurately set equal to the mass of the electron. If one wishes to consider the case of an an electron bound to a nucleus with Z protons one lets $e^2 \to Ze^2$ in $H^{(0)}$. The Bohr radius is the length scale build from $\hbar, m$, and e^2

$$a_0 \equiv \frac{\hbar^2}{me^2} \ \sim 53\,\text{pm}. \tag{2.1.2}$$

The energy levels are enumerated using a *principal* quantum number n, an integer that must be greater or equal to one:

$$E_n = -\frac{e^2}{2a_0}\frac{1}{n^2}\,, \quad n = 1, 2, \ldots\,. \tag{2.1.3}$$

Note that $H^{(0)}$ is a non-relativistic Hamiltonian: the speed of light does not enter in it, and the kinetic term is that of Newtonian mechanics. The energy scale relevant to the

bound state spectrum can be better appreciated using the speed of light to consider both the fine structure constant and the rest energy of the electron. The fine structure constant is given by

$$\alpha \equiv \frac{e^2}{\hbar c} \simeq \frac{1}{137}, \tag{2.1.4}$$

and the rest energy of the electron is mc^2. Then,

$$\frac{e^2}{a_0} = \frac{me^4}{\hbar^2} = \frac{m\alpha^2\hbar^2c^2}{\hbar^2} = \alpha^2 mc^2. \tag{2.1.5}$$

This states that the energy scale of hydrogen bound states is a factor of α^2 smaller than the rest energy of the electron, that is, about 19000 times smaller. We can thus rewrite the possible energies as:

$$E_n = -\tfrac{1}{2}\alpha^2 mc^2 \frac{1}{n^2}. \tag{2.1.6}$$

The typical momentum in the hydrogen atom is

$$p \simeq \frac{\hbar}{a_0} = \frac{me^2}{\hbar} = \frac{e^2}{\hbar c}mc \quad \rightarrow \quad p \simeq \alpha(mc), \tag{2.1.7}$$

which, written as $p \simeq m(\alpha c)$ says that the typical velocity is $v \simeq \alpha c$, which is low enough that the non-relativistic approximation is fairly accurate. Finally, we note that

$$a_0 = \frac{\hbar^2}{m\,\alpha\hbar c} = \frac{\hbar}{mc}\frac{1}{\alpha} = \frac{\lambda\!\!\!^{-}}{\alpha}, \tag{2.1.8}$$

which says that the Bohr radius is over a hundred times bigger than the (reduced) Compton wavelength of the electron.

The degeneracy of the hydrogen atom spectrum is completely quantified by the relation

$$n = N + \ell + 1. \tag{2.1.9}$$

Here $N \geq 0$ is the degree of a polynomial in r that appears in a wavefunction where the leading dependence on r near the origin is factored out. The quantum number $\ell \geq 0$ is the angular momentum of the state. For each fixed n, you can see that the number ℓ ranges from zero to $n-1$. And for each fixed ℓ the eigenvalue of L_z is $m\hbar$ with m ranging from $-\ell$ up to ℓ:

$$n = 1, 2, \ldots \qquad \ell = 0, 1, \ldots, n-1$$

$$m = -\ell, \ldots, \ell \qquad \#\text{ of states with energy } E_n = \sum_{\ell=0}^{n-1}(2\ell+1) = n^2$$

The states of hydrogen are shown in this energy diagram, which is not drawn to scale,

	S $\ell=0$	P $\ell=1$	D $\ell=2$	F $\ell=3$
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$
$n=4$	$N=3$	$N=2$	$N=1$	$N=0$
$n=3$	$N=2$	$N=1$	$N=0$	
$n=2$	$N=1$	$N=0$		
$n=1$	$N=0$			

The table features the commonly used notation where capital letters are used to denote the various values of the orbital angular momentum ℓ. If we have L denote the generic capital letter for angular momentum we have $L(\ell)$ where

$$L(\ell=0)=S\,,\quad L(\ell=1)=P\,,\quad L(\ell=2)=D\,,\quad L(\ell=3)=F\,,\ldots\,. \tag{2.1.10}$$

Thus, for example, an S state is a state with $\ell=0$, a P state is a state with $\ell=1$, and a D state is a state with $\ell=2$.

Any hydrogen eigenstate specified by the three quantum numbers n,ℓ,m, because, as it follows from (2.1.9), the value of N is then fixed. The wavefunction takes the form

$$\psi_{n,\ell,m}(\mathbf{x})=A\left(\frac{r}{a_0}\right)^{\ell}\cdot\left(\text{Polynomial in }\frac{r}{a_0}\text{ of degree }N\right)\cdot e^{-\frac{r}{na_0}}Y_{\ell,m}(\theta,\phi)\,, \tag{2.1.11}$$

where A is a normalization constant and $N=n-(\ell+1)$. If you look at the wavefunction, the value of n can be read from the exponential factor. The value of ℓ can be read from the radial prefactor, or from the spherical harmonic. The value of m can be read from the spherical harmonic. For the ground state $n=1$, $\ell=0$ and $m=0$. The normalized wavefunction is

$$\psi_{1,0,0}(r)\;=\;\frac{1}{\sqrt{\pi a_0^3}}\,e^{-\frac{r}{a_0}}\,. \tag{2.1.12}$$

Comments:

1. There are n^2 degenerate states at any energy level with principal quantum number n. This degeneracy explained by the existence of a conserved quantum Runge-Lenz vector. For a given n the states with various ℓ's correspond, in the semiclassical picture, to orbits of different eccentricity but the same semi-major axis. The orbit with $\ell=0$ is the most eccentric one and the orbit with maximum $\ell=n-1$ is the most circular one.

2. For each fixed value of ℓ, the states have increasing N as we move up in energy. The number N is the number of nodes in the solution of the radial equation, that's why it is the degree of the polynomial in r that features in the wavefunction (2.1.11).

3. The analysis of $H^{(0)}$ so far ignored electron spin. Since the electron is a spin one-half particle there is an extra degeneracy: each of the $H^{(0)}$ eigenstates is really two degenerate states, one with the electron spin up and the other with the electron spin down. These states are degenerate because $H^{(0)}$ has no spin dependence.

4. We will have to supplement $H^{(0)}$ with terms that correspond to corrections that arise from relativity and from the spin of the electron. This will be the main subject of the following analysis. It will determine the *fine-structure* of the hydrogen atom. The corrections will break much of the degeneracy of the spectrum.

5. In order to understand better the spectrum and the properties of the Hydrogen atom one can apply an electric field, leading to the *Stark* effect or a magnetic field, leading to the *Zeeman* effect. These external fields are represented by extra terms in the hydrogen atom Hamiltonian.

Let us now discuss two different choices of basis states for the hydrogen atom, both of which include the electron spin properly.

Recall that, in general, for a multiplet of angular momentum j, we have states (j, m_j), with m_j running from $-j$ to j in integer steps. All states in the multiplet are $\hat{\mathbf{J}}^2$ eigenstates with eigenvalue $\hbar^2 j(j+1)$ and, for each state, $\hbar m_j$ is the eigenvalue of $\hat{J}_z$.

Because the electron has spin one half, its states are labeled as

$$(s, m_s)\,, \quad \text{with} \quad s = \tfrac{1}{2}\,, \quad m_s = \pm\tfrac{1}{2}\,. \tag{2.1.13}$$

In the hydrogen atom the angular momentum ℓ can take different values, but the spin of the electron is always one-half. As a result, the label s is often omitted, and we usually only record the value of m_s. For hydrogen basis states we thus have quantum numbers n, ℓ, m_ℓ, *and* m_s. To avoid confusion, we have added the ℓ subscript to m_ℓ, thus emphasizing that this is the azimuthal quantum number for orbital angular momentum. Since we are not combining the electron spin to its orbital angular momentum, the states form the "uncoupled basis":

$$\boxed{\text{Uncoupled basis quantum numbers:} \quad (n, \ell, m_\ell, m_s)\,.} \tag{2.1.14}$$

The states are completely specified by these quantum numbers. As we let those quantum numbers run over all possible values we obtain an orthonormal basis of states.

It is often useful to use an alternative basis where the states are eigenstates of $\hat{\mathbf{J}}^2$ and $\hat{J}_z$, where the total angular momentum $\hat{\mathbf{J}}$ is obtained by adding the orbital angular momentum $\hat{\mathbf{L}}$ to the spin angular momentum $\hat{\mathbf{S}}$:

$$\hat{\mathbf{J}} \;=\; \hat{\mathbf{L}} + \hat{\mathbf{S}}\,. \tag{2.1.15}$$

When we form $\ell \otimes s$ we are tensoring a a full ℓ multiplet to an s multiplet (here, of course, $s = 1/2$). All states in $\ell \otimes s$ are eigenstates of $\hat{\mathbf{L}}^2$ and eigenstates of $\hat{\mathbf{S}}^2$, so ℓ and s are good (constant) quantum numbers for all j multiplets that arise in the tensor product. Each j multiplet has states with quantum numbers (j, m_j).

The coupled basis is one where states are organized into j multiplets. While states are no longer $\hat{L}_z$ nor $\hat{S}_z$ eigenstates they are still $\hat{\mathbf{L}}^2$ eigenstates, thus the ℓ quantum number survives. The coupled basis quantum numbers are therefore

$$\boxed{\text{Coupled basis quantum numbers:} \quad (n, \ell, j, m_j)\,.} \tag{2.1.16}$$

The (m_ℓ, m_s) quantum numbers of the uncoupled basis have been traded for (j, m_j) quantum numbers and we have kept the n, ℓ quantum numbers. The coupled states are linear combinations of uncoupled states that involve different values of m_ℓ and m_s, those combinations that yield the same value of $m_j = m_\ell + m_s$.

To find the list of coupled basis states we must tensor *each* ℓ multiplet in the hydrogen atom spectrum with the spin doublet $\frac{1}{2}$. The rules of addition of angular momentum imply that we find two j multiplets:

$$\ell \otimes \tfrac{1}{2} \;=\; (j = \ell + \tfrac{1}{2}) \oplus (j = \ell - \tfrac{1}{2})\,. \tag{2.1.17}$$

For $\ell = 0$, we only obtain a $j = 1/2$ multiplet. We use the notation L_j for the coupled multiplets, with $L = S, P, D, F$ for $\ell = 0, 1, 2$, and 3 (see (2.1.10). The change of basis is summarized by the replacements

$$\ell \otimes \tfrac{1}{2} \quad \to \quad L(\ell)_{j=\ell+\frac{1}{2}} \oplus L(\ell)_{j=\ell-\frac{1}{2}} \tag{2.1.18}$$

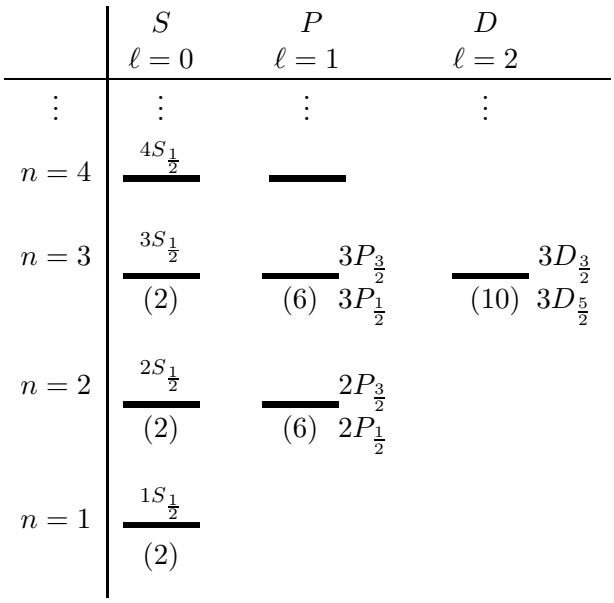
or more explicitly,

$$\begin{aligned} 0 \otimes \tfrac{1}{2} \quad &\to \quad S_{\frac{1}{2}} \\ 1 \otimes \tfrac{1}{2} \quad &\to \quad P_{\frac{3}{2}} \oplus P_{\frac{1}{2}} \\ 2 \otimes \tfrac{1}{2} \quad &\to \quad D_{\frac{5}{2}} \oplus D_{\frac{3}{2}} \\ 3 \otimes \tfrac{1}{2} \quad &\to \quad F_{\frac{7}{2}} \oplus F_{\frac{5}{2}} \end{aligned} \tag{2.1.19}$$

Thus, by the time we combine with electron spin, each $\ell = 0$ state gives one $j = \frac{1}{2}$ multiplet, each $\ell = 1$ state gives $j = \frac{3}{2}$ and $j = \frac{1}{2}$ multiplets, each $\ell = 2$ state gives $j = \frac{5}{2}$ and $j = \frac{3}{2}$ multiplets, and so on. For hydrogen, the principal quantum number is placed ahead to denote the coupled multiplets by

$$\text{Coupled basis notation for multiplets:} \quad \boxed{nL_j} \tag{2.1.20}$$

Using this notation for coupled basis multiplets the diagram of hydrogen atom energy eigenstates becomes:



The number of states is indicated in parenthesis.

2.2 The Pauli equation

In the hydrogen atom the spin-orbit coupling arises because the electron is moving in the electric field of the proton. Since the electron is moving relative to the frame where we have a static electric field, the electron also sees a magnetic field $\mathbf{B}$. The spin-orbit coupling is the coupling $-\boldsymbol{\mu}\cdot\mathbf{B}$ of that magnetic field to the magnetic dipole moment $\boldsymbol{\mu}$ of the electron.

We have discussed before, in the context of the Stern-Gerlach experiment, the value of the magnetic dipole moment of the electron. Recall the logic we used. In Gaussian units, the classical magnetic moment of a planar current loop is given by $\boldsymbol{\mu} = \frac{I}{c}\mathbf{a}$, where I is the current and $\mathbf{a}$ is the area vector associated with the loop. From this one quickly derives that for a uniformly rotating particle with charge q and mass m the magnetic moment is

$$\boldsymbol{\mu} = \frac{q}{2mc}\mathbf{L}\,, \tag{2.2.1}$$

where $\mathbf{L}$ is the angular momentum due to the rotation. For an elementary particle, this motivates the following relation between the spin angular momentum operator $\hat{\mathbf{S}}$ and the magnetic moment

$$\boldsymbol{\mu} \;=\; g\,\frac{q}{2mc}\,\hat{\mathbf{S}} \tag{2.2.2}$$

where g is a factor that is added to parameterize our ignorance; after all there is no reason why the classically motivated formula for the magnetic dipole should hold in the quantum domain of spin. As it turns out, for an electron one has $g = 2$. Since $q = -e$ for an electron,

we have

$$\boldsymbol{\mu} \;=\; 2\,\frac{-e}{2m_e c}\,\hat{\mathbf{S}} \;=\; -2\,\frac{e\hbar}{2m_e c}\,\frac{\hat{\mathbf{S}}}{\hbar} \;=\; -2\,\frac{e\hbar}{2m_e c}\,\tfrac{1}{2}\boldsymbol{\sigma} \;=\; -\,\frac{e\hbar}{2m_e c}\,\boldsymbol{\sigma}\,. \tag{2.2.3}$$

For numerical applications we note that the *Bohr magneton* μ_B is defined by

$$\mu_B = \frac{e\hbar}{2m_e c} \;\simeq\; 9.274\times 10^{-21}\,\frac{\text{erg}}{\text{gauss}} \;=\; 5.79\times 10^{-9}\,\frac{\text{eV}}{\text{gauss}}\,. \tag{2.2.4}$$

(for SI values use Tesla $= 10^4$ gauss). The coupling of an electron to an external magnetic field is therefore represented by a Hamiltonian H_B given by

$$\boxed{H_B \;=\; -\boldsymbol{\mu}\cdot\mathbf{B} \;=\; \frac{e\hbar}{2m_e c}\,\boldsymbol{\sigma}\cdot\mathbf{B}\,.} \tag{2.2.5}$$

Our goal now is to show that this coupling, and its associated prediction of $g = 2$, arises naturally from the non-relativistic Pauli equation for an electron.

Consider first the time-independent Schrödinger equation for a free particle:

$$\frac{\hat{\mathbf{p}}^2}{2m}\psi \;=\; E\,\psi\,. \tag{2.2.6}$$

Since a spin one-half particle has two degrees of freedom, usually assembled into a column vector χ, the expected equation for a free spin one-half particle is

$$\frac{\hat{\mathbf{p}}^2}{2m}\chi \;=\; E\,\chi \quad \text{with} \quad \chi = \begin{pmatrix}\chi_1\\ \chi_2\end{pmatrix}\,. \tag{2.2.7}$$

One sometimes calls χ a Pauli spinor. Note there's an implicit two-by-two identity matrix $\mathbb{1}_{2\times 2}$ in the Hamiltonian

$$H \;=\; \frac{\hat{\mathbf{p}}^2}{2m}\,\mathbb{1}_{2\times 2}\,. \tag{2.2.8}$$

We can *rewrite* this Hamiltonian using Pauli matrices if we recall the identity

$$(\boldsymbol{\sigma}\cdot\mathbf{a})(\boldsymbol{\sigma}\cdot\mathbf{b}) \;=\; \mathbf{a}\cdot\mathbf{b}\,\mathbb{1}_{2\times 2} + i\boldsymbol{\sigma}\cdot(\mathbf{a}\times\mathbf{b})\,, \tag{2.2.9}$$

valid for arbitrary vector operators $\mathbf{a}$ and $\mathbf{b}$. Taking $\mathbf{a} = \mathbf{b} = \hat{\mathbf{p}}$, with $\hat{\mathbf{p}}$ the momentum operator, and recognizing that $\hat{\mathbf{p}}\times\hat{\mathbf{p}} = \mathbf{0}$, we have

$$(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})\cdot(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}) \;=\; \hat{\mathbf{p}}^2\,\mathbb{1}_{2\times 2}\,. \tag{2.2.10}$$

This means that the Hamiltonian (2.2.8) can be rewritten as

$$H \;=\; \frac{1}{2m}\,(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})\,. \tag{2.2.11}$$

So far, this is all just rewriting with no change in physics. But new things happen when we the particle is charged and we couple it to external electromagnetic fields. The quantum mechanical rule is that this inclusion can be taken care with the replacement

$$\boxed{\hat{\mathbf{p}} \;\to\; \hat{\boldsymbol{\pi}} \;\equiv\; \hat{\mathbf{p}} - \frac{q}{c}\mathbf{A}\,.} \tag{2.2.12}$$

Here q is the charge of the particle and $\mathbf{A}$ is the external vector potential, a function of position that becomes an operator $\mathbf{A}(\hat{\mathbf{x}})$ since position is an operator. In addition, if there is a electromagnetic scalar potential Φ it contributes an additional term $q\Phi(\hat{\mathbf{x}})$ to the Hamiltonian.

With the replacement (2.2.12) applied to the Hamiltonian (2.2.11), and the inclusion of the coupling to the scalar potential, we get the **Pauli Hamiltonian**:

$$\boxed{H_{\text{Pauli}} \;=\; \frac{1}{2m}\,(\boldsymbol{\sigma}\cdot\hat{\boldsymbol{\pi}})\,(\boldsymbol{\sigma}\cdot\hat{\boldsymbol{\pi}}) + q\Phi(\hat{\mathbf{x}})\,.} \tag{2.2.13}$$

This time, using the identity (2.2.9), the second term survives

$$H_{\text{Pauli}} \;=\; \frac{1}{2m}\left[(\hat{\boldsymbol{\pi}}\cdot\hat{\boldsymbol{\pi}})\mathbb{1} + i\boldsymbol{\sigma}\cdot(\hat{\boldsymbol{\pi}}\times\hat{\boldsymbol{\pi}})\right] + q\Phi(\hat{\mathbf{x}})\,. \tag{2.2.14}$$

We have $\hat{\boldsymbol{\pi}}\times\hat{\boldsymbol{\pi}} \neq \mathbf{0}$ because the various π_i do not commute. Note that the replacement (2.2.12) applied to the original Hamiltonian (2.2.8) would not have given us the $\hat{\boldsymbol{\pi}}\times\hat{\boldsymbol{\pi}}$ term.

To evaluate that term we use

$$(\hat{\boldsymbol{\pi}}\times\hat{\boldsymbol{\pi}})_k \;=\; \epsilon_{ijk}\hat{\pi}_i\hat{\pi}_j \;=\; \tfrac{1}{2}\epsilon_{ijk}[\hat{\pi}_i,\hat{\pi}_j]\,. \tag{2.2.15}$$

The commutator here is

$$[\,\pi_i\,,\,\pi_j\,] \;=\; \left[\,p_i - \frac{q}{c}A_i\,,\,p_j - \frac{q}{c}\,A_j\,\right]\,. \tag{2.2.16}$$

As usual, the $\hat{\mathbf{p}}$ components can be thought of as derivatives acting on the spatially dependent components of $\mathbf{A}$. Moreover, the A_i's being only functions of position, commute among themselves and we have

$$[\,\pi_i\,,\,\pi_j\,] \;=\; -\frac{\hbar}{i}\frac{q}{c}\,(\partial_i A_j - \partial_j A_i) = \frac{i\hbar q}{c}\,(\partial_i A_j - \partial_j A_i)\,. \tag{2.2.17}$$

Therefore, back in (2.2.16)

$$(\boldsymbol{\pi}\times\boldsymbol{\pi})_k \;=\; \tfrac{1}{2}\epsilon_{ijk}\frac{i\hbar q}{c}\,(\partial_i A_j - \partial_j A_i) \;=\; \frac{i\hbar q}{c}\epsilon_{ijk}\partial_i A_j = \frac{i\hbar q}{c}\,(\nabla\times A)_k\,, \tag{2.2.18}$$

leading to the elegant result:

$$\hat{\boldsymbol{\pi}}\times\hat{\boldsymbol{\pi}} \;=\; \frac{i\hbar q}{c}\,\mathbf{B}\,. \tag{2.2.19}$$

This equation is a bit reminiscent of the equation $\hat{\mathbf{L}} \times \hat{\mathbf{L}} = i\hbar\hat{\mathbf{L}}$, for angular momentum.

Back in the Pauli Hamiltonian (2.2.14), leaving identity matrices implicit, and setting $q = -e$, we find

$$\begin{aligned} H_{\text{Pauli}} &= \frac{1}{2m}\left(\hat{\mathbf{p}} + \frac{e}{c}\mathbf{A}\right)^2 + \frac{i}{2m}\frac{i\hbar q}{c}\boldsymbol{\sigma}\cdot\mathbf{B} - e\Phi(\hat{\mathbf{x}}) \\ &= \frac{1}{2m}\left(\hat{\mathbf{p}} + \frac{e}{c}\mathbf{A}\right)^2 + \frac{e\hbar}{2mc}\boldsymbol{\sigma}\cdot\mathbf{B} - e\Phi(\hat{\mathbf{x}})\,. \end{aligned} \tag{2.2.20}$$

The second term in this expanded Pauli Hamiltonian gives the coupling of the electron spin to the magnetic field and agrees precisely with the expected coupling (2.2.5). We thus see that the Pauli equation predicts the $g = 2$ value in the electron magnetic moment.

2.3 The Dirac equation

While the Pauli equation incorporates correctly the coupling of the electron spin to electromagnetic fields, it is not a relativistic equation. As discovered by Dirac, to include relativity one has to work with matrices and the Pauli spinor must be upgraded to a four-component spinor. The analysis begins with the familiar relation between relativistic energies and momenta

$$E^2 - \mathbf{p}^2c^2 = m^2c^4 \quad \rightarrow \quad E = \sqrt{\mathbf{p}^2c^2 + m^2c^4} \tag{2.3.1}$$

This suggests that a relativistic Hamiltonian for a free particle could take the form

$$H = \sqrt{\hat{\mathbf{p}}^2c^2 + m^2c^4}\,, \tag{2.3.2}$$

with associated Schrödinger equation

$$i\hbar\frac{\partial\psi}{\partial t} = \sqrt{\hat{\mathbf{p}}^2c^2 + m^2c^4}\,\psi\,. \tag{2.3.3}$$

It is not clear how to treat the square root so, at least for small velocities $p \ll mc$, the Hamiltonian can be expanded:

$$\begin{aligned} H &= mc^2\sqrt{1 + \frac{\hat{\mathbf{p}}^2}{m^2c^2}} = mc^2\left[1 + \frac{\hat{\mathbf{p}}^2}{2m^2c^2} - \frac{1}{8}\left(\frac{\hat{\mathbf{p}}^2}{m^2c^2}\right)^2 + \ldots\right] \\ &= mc^2 + \frac{\hat{\mathbf{p}}^2}{2m} - \frac{1}{8}\frac{\hat{\mathbf{p}}^4}{m^3c^2} + \ldots \end{aligned} \tag{2.3.4}$$

If we ignore the constant rest mass, the first term is the familiar non-relativistic Hamiltonian, and the next term is the first nontrivial relativistic correction. For small momenta we will treat that term as a perturbation.

More elegantly, Dirac wanted to find a Hamiltonian linear in momenta and without square roots. This would be possible if one could write the relativistic energy as the square of a linear function of the momentum:

$$c^2\hat{\mathbf{p}}^2 + m^2c^4 = (c\boldsymbol{\alpha}\cdot\hat{\mathbf{p}} + \beta mc^2)^2 = (c\alpha_1\hat{p}_1 + c\alpha_2\hat{p}_2 + c\alpha_3\hat{p}_3 + \beta mc^2)^2\,. \tag{2.3.5}$$

Expanding the right-hand side and equating coefficients one finds that the following must hold

$$\begin{aligned} &\alpha_1^2 = \alpha_2^2 = \alpha_3^2 = \beta^2 = 1\,, \\ &\alpha_i\alpha_j + \alpha_j\alpha_i = \{\alpha_i, \alpha_j\} = 0\,, \quad i \neq j\,, \\ &\alpha_i\beta + \beta\alpha_i = \{\alpha_i, \beta\} = 0\,. \end{aligned} \tag{2.3.6}$$

The relations on the second and third lines imply that α's and β's can't be numbers, because they would have to be zero. It turns out that α's and β's are four-by-four hermitian matrices:

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix}\,, \quad \beta = \begin{pmatrix} \mathbb{1} & 0 \\ 0 & -\mathbb{1} \end{pmatrix}\,. \tag{2.3.7}$$

Using (2.3.5), the Dirac Hamiltonian is simply the linear function of momentum that is the square root of $c^2\hat{\mathbf{p}}^2 + m^2c^4$. We thus have

$$H_{\text{Dirac}} \;=\; c\boldsymbol{\alpha}\cdot\mathbf{p} + \beta mc^2\,. \tag{2.3.8}$$

The Dirac equation is

$$i\hbar\frac{\partial\Psi}{\partial t} \;=\; \left(c\boldsymbol{\alpha}\cdot\mathbf{p} + \beta mc^2\right)\Psi\,, \tag{2.3.9}$$

where Ψ is a Dirac spinor, a four-component column vector that can be thought to be composed by two two-component Pauli spinors χ and η:

$$\Psi = \begin{pmatrix} \chi \\ \eta \end{pmatrix}\,, \qquad \chi = \begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix}\,, \qquad \eta = \begin{pmatrix} \eta_1 \\ \eta_2 \end{pmatrix}\,. \tag{2.3.10}$$

The coupling to electromagnetic fields is done as before

$$i\hbar\frac{\partial\Psi}{\partial t} = \Big[\; c\boldsymbol{\alpha}\cdot\Big(\hat{\mathbf{p}} + \frac{e}{c}\mathbf{A}\Big) + \;\beta mc^2 \;+\; V(r)\;\Big]\Psi\,, \tag{2.3.11}$$

where the coupling of the electron to the scalar potential $\Phi(r)$ is included via

$$V(r) = -e\Phi(r) = -\frac{e^2}{r}\,. \tag{2.3.12}$$

The great advantage of the Dirac equation (2.3.11) is that the corrections to the hydrogen Hamiltonian $H^{(0)}$ can be derived systematically by finding the appropriate Hamiltonian H that acts on the Pauli spinor χ. The analysis, can be done with $\mathbf{A} = 0$, since the stationary proton creates no vector potential. The result of the analysis shows that

$$H\chi = E\chi\,, \tag{2.3.13}$$

where:

$$\boxed{H \;=\; \underbrace{\frac{\hat{\mathbf{p}}^2}{2m} + V}_{H^{(0)}} \;-\; \underbrace{\frac{\hat{\mathbf{p}}^4}{8m^3c^2}}_{\delta H_{\text{rel.}}} \;+\; \underbrace{\frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\mathbf{S}\cdot\mathbf{L}}_{\delta H_{\text{spin-orbit}}} \;+\; \underbrace{\frac{\hbar^2}{8m^2c^2}\nabla^2 V}_{\delta H_{\text{Darwin}}}\,.} \tag{2.3.14}$$

The first correction is the relativistic energy correction anticipated earlier. The second is the spin-orbit coupling, and the third is the *Darwin* correction, that as we shall see affects only $\ell = 0$ states.

Recall that the energy scale for $H^{(0)}$ eigenstates is $\alpha^2 mc^2$. We will now see that *all the above energy corrections are of order* $\alpha^4 mc^2$ thus smaller by a factor of $\alpha^2 \simeq \frac{1}{19000}$ than the zeroth-order energies. This suggests that for the hydrogen atom, the role of the unit-free parameter λ of perturbation theory is taken by the fine structure constant: $\lambda \sim \alpha^2$. Of course, in reality we cannot adjust the value of α^2 nor we can take it to zero.

For the relativistic correction, recalling that $p \simeq \alpha\, mc$, we indeed have

$$\delta H_{\text{rel.}} \;= -\frac{\mathbf{p}^4}{8m^3c^2} \sim\; -\alpha^4 mc^2\,. \tag{2.3.15}$$

For spin-orbit we first rewrite the term, using

$$\frac{1}{r}\frac{dV}{dr} = \frac{1}{r}\frac{d}{dr}\left(-\frac{e^2}{r}\right) = \frac{e^2}{r^3}\,, \tag{2.3.16}$$

so that

$$\delta H_{\text{spin-orbit}} \;=\; \frac{e^2}{2m^2c^2}\frac{1}{r^3}\,\mathbf{S}\cdot\mathbf{L}\,. \tag{2.3.17}$$

For an estimate we set $\mathbf{S}\cdot\mathbf{L} \sim \hbar^2$, $r \sim a_0$, and recall that $a_0 = \frac{\hbar}{mc}\frac{1}{\alpha}$:

$$\delta H_{\text{spin-orbit}} \;\sim\; \frac{e^2}{m^2c^2}\,\frac{\hbar^2}{a_0^3} = \;\frac{\alpha\,\hbar c}{m^2c^2}\,\frac{\hbar^2}{a_0^3} \;= \alpha\Big(\frac{\hbar}{mca_0}\Big)^3 mc^2 \;=\; \alpha^4\, mc^2\,. \tag{2.3.18}$$

We can evaluate the Darwin term using $V = -e^2/r$:

$$\delta H_{\text{Darwin}} \;=\; -\frac{e^2\hbar^2}{8m^2c^2}\nabla^2\left(\frac{1}{r}\right) \;= \frac{e^2\hbar^2}{8m^2c^2}(-4\pi\delta(\mathbf{r})) \;= \frac{\pi}{2}\frac{e^2\hbar^2}{m^2c^2}\delta(\mathbf{r})\,. \tag{2.3.19}$$

To estimate this correction note that, due to the δ function the the integral in the expectation value will introduce a factor $|\psi(\mathbf{0})|^2 \sim a_0^{-3}$. We will therefore have

$$\delta H_{\text{Darwin}} \;\sim\; \frac{e^2\hbar^2}{m^2c^2a_0^3} \;\sim\; \alpha^4\, mc^2\,, \tag{2.3.20}$$

as this is exactly the same combination of constants that we had for spin orbit above.

2.4 Fine structure of hydrogen

The fine structure of hydrogen is the spectrum of the atom once one takes into account the corrections indicated in (2.3.14). After the partial simplifications considered above we have

$$H \;=\; \underbrace{\frac{\hat{\mathbf{p}}^2}{2m} + V}_{H^{(0)}} \;-\; \underbrace{\frac{\hat{\mathbf{p}}^4}{8m^3c^2}}_{\delta H_{\text{rel.}}} \;+\; \underbrace{\frac{e^2}{2m^2c^2}\frac{\mathbf{S}\cdot\mathbf{L}}{r^3}}_{\delta H_{\text{spin-orbit}}} \;+\; \underbrace{\frac{\pi}{2}\frac{e^2\hbar^2}{m^2c^2}\delta(\mathbf{r})}_{\delta H_{\text{Darwin}}}\,. \tag{2.4.21}$$

We will study each of these terms separately and then combine our results to give the fine structure of hydrogen. There are further smaller corrections that we will not examine here, such as hyperfine splitting and Lamb effect.

2.4.1 Darwin correction

Let us now evaluate the Darwin correction. Since this interaction has a delta function at the origin, the first order correction to the energy vanishes unless the wavefunction is non-zero at the origin. This can only happen for nS states. There is no need to use the apparatus of degenerate perturbation theory. Indeed, for fixed n there are two orthogonal $\ell = 0$ states, one with electron spin up and one with electron spin down. While these states are degenerate, the Darwin perturbation commutes with spin and is therefore diagonal in the two-dimensional subspace. There is no need to include the spin in the calculation and we have

$$E^{(1)}_{n00,\text{Darwin}} \;=\; \langle\psi_{n00}|\delta H_{\text{Darwin}}|\psi_{n00}\rangle \;=\; \frac{\pi}{2}\frac{e^2\hbar^2}{m^2c^2}|\psi_{n00}(\mathbf{0})|^{\mathbf{2}}\,. \tag{2.4.22}$$

As is shown in the homework, the radial equation can be used to determine the value of the nS wavefunctions at the origin. You will find that

$$|\psi_{n00}(0)|^2 \;=\; \frac{1}{\pi\, n^3 a_0^3}\,. \tag{2.4.23}$$

As a result

$$E^{(1)}_{n00,\text{Darwin}} \;=\; \frac{e^2\hbar^2}{2m^2c^2}\frac{1}{a_0^3 n^3} \;=\; \alpha^4(mc^2)\frac{1}{2n^3}\;. \tag{2.4.24}$$

This completes the evaluation of the Darwin correction

The Darwin term in the Hamiltonian arises from the elimination of one of the two two-component spinors in the Dirac equation. As we will show now such a correction would arise from a nonlocal correction to the potential energy term. It is as if the electron had grown from point-like to a ball with radius of order its Compton wavelength $\frac{\hbar}{m_e c}$. The potential energy due to the field of the proton must then be calculated by integrating the varying electric potential over the charge distribution of the electron. While a simple estimate of this nonlocal potential energy does reproduce the Darwin correction rather closely, one must not reach the conclusion that the electron is no longer a point particle. Still the fact remains that in a relativistic treatment of an electron, its Compton wavelength is relevant and is physically the shortest distance an electron can be localized.

The potential energy $V(\mathbf{r})$ of the electron, as a point particle, is the product of the electron charge $(-e)$ times the electric potential $\Phi(\mathbf{r})$ created by the proton:

$$V(\mathbf{r}) = (-e)\Phi(\mathbf{r}) = (-e)\,\frac{e}{r}\,. \tag{2.4.25}$$

Let us call $\widetilde{V}(\mathbf{r})$ the potential energy when the electron is a charge distribution centered at a point $\mathbf{r}$ with $|\mathbf{r}| = r$ (see Figure 2.1). This energy is obtained by integration over the

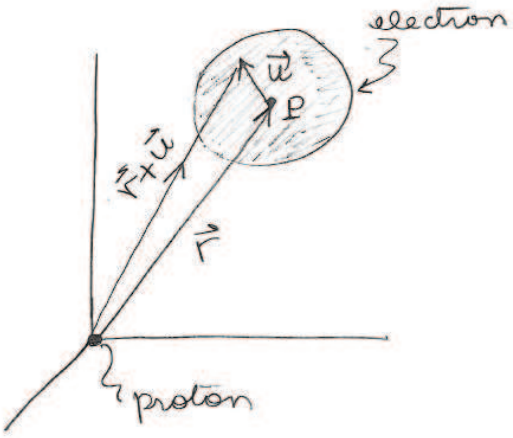


Figure 2.1: A Darwin type correction to the energy arises if the electron charge is smeared over a region of size comparable to its Compton wavelength. Here the center of the spherically symmetric electron cloud is at P and the proton is at the origin. The vector $\mathbf{u}$ is radial relative to the center of the electron.

electron distribution. Using the vector $\mathbf{u}$ to define position relative to the center P of the electron, and letting $\rho(\mathbf{u})$ denote the position dependent charge density, we have

$$\widetilde{V}(\mathbf{r}) \;=\; \int_{\text{electron}} d^3\mathbf{u}\,\rho(\mathbf{u})\mathbf{\Phi}(\mathbf{r}+\mathbf{u})\,, \tag{2.4.26}$$

where, as shown in the Figure, $\mathbf{r}+\mathbf{u}$ is the position of the integration point, measured relative to the proton at the origin. It is convenient to write the charge density in terms of a normalized function ρ_0:

$$\rho(\mathbf{u}) \;=\; -e\,\rho_0(\mathbf{u}) \quad\rightarrow\quad \int_{\text{electron}} d^3\mathbf{u}\,\rho_0(\mathbf{u}) = 1\,, \tag{2.4.27}$$

which guarantees that the integral of ρ over the electron is indeed $(-e)$. Recalling that $-e\Phi(\mathbf{r}+\mathbf{u}) = V(\mathbf{r}+\mathbf{u})$ we now rewrite (2.4.26) as

$$\widetilde{V}(\mathbf{r}) \;=\; \int_{\text{electron}} d^3\mathbf{u}\,\rho_0(\mathbf{u})V(\mathbf{r}+\mathbf{u})\,. \tag{2.4.28}$$

This equation has a clear interpretation: the potential energy is obtained as a weighted integral of potential due to the proton over the extended electron. If the electron charge would be perfectly localized, $\rho_0(\mathbf{u}) = \delta(\mathbf{u})$ and $\tilde{V}(\mathbf{r})$ would just be equal to $V(\mathbf{r})$. We will assume that the distribution of charge is spherically symmetric, so that

$$\rho_0\,(\mathbf{u}) = \rho_0(u)\,. \tag{2.4.29}$$

To evaluate (2.4.31), we first do a Taylor expansion of the potential that enters the integral about the point $\mathbf{u} = 0$:

$$V(\mathbf{r}+\mathbf{u}) = V(\mathbf{r}) + \sum_i \partial_i V\Big|_{\mathbf{r}} u_i + \frac{1}{2}\sum_{i,j} \partial_i\partial_j V\Big|_{\mathbf{r}} u_i u_j \ + \ \ldots \tag{2.4.30}$$

All derivatives here are evaluated at the center of the electron. Plugging back into the integral (2.4.31) and dropping the subscript 'electron' we have

$$\widetilde{V}(\mathbf{r}) \ = \ \int d^3\mathbf{u}\,\rho_0(\mathbf{u})\Big(V(\mathbf{r}) + \sum_i \partial_i V\Big|_{\mathbf{r}} u_i + \frac{1}{2}\sum_{i,j} \partial_i\partial_j V\Big|_{\mathbf{r}} u_i u_j \ + \ \ldots\Big)\,. \tag{2.4.31}$$

All $\mathbf{r}$ dependent functions can be taken out of the integrals. Recalling that the integral of ρ_0 over volume is one, we get

$$\tilde{V}(\mathbf{r}) \ = \ V(\mathbf{r}) \ + \ \sum_i \partial_i V\Big|_{\mathbf{r}} \int d^3\mathbf{u}\,\rho_0(\mathbf{u})\,\rho_i \ + \ \tfrac{1}{2}\sum_{i,j} \partial_i\partial_j V\Big|_{\mathbf{r}} \int d^3\mathbf{u}\,\rho_0(\mathbf{u})\,u_i u_j + \ldots \tag{2.4.32}$$

Due to spherical symmetry the first integral vanishes and the second takes the form

$$\int d^3\mathbf{u}\,\rho_0(\mathbf{u})\,u_i u_j \ = \ \tfrac{1}{3}\delta_{ij}\int d^3\mathbf{u}\,\rho_0(\mathbf{u})\,u^2\,. \tag{2.4.33}$$

Indeed the integral must vanish for $i \neq j$ and must take equal values for $i = j = 1, 2, 3$. Since $u^2 = u_1^2 + u_2^2 + u_3^2$, the result follows. Using this we get

$$\begin{aligned} \tilde{V}(\mathbf{r}) \ &= \ V(\mathbf{r}) \ + \ \tfrac{1}{2}\sum_i \partial_i\partial_i V\Big|_{\mathbf{r}} \ \tfrac{1}{3}\int d^3\mathbf{u}\,f(\mathbf{u})\,\rho^2 + \ldots \\ &= \ V(\mathbf{r}) \ + \ \tfrac{1}{6}\nabla^2 V\int d^3\mathbf{u}\,\rho_0(\mathbf{u})\,u^2 \ + \ \ldots\,. \end{aligned} \tag{2.4.34}$$

The second term represents the correction δV to the potential energy:

$$\delta V \ = \ \tfrac{1}{6}\nabla^2 V\int d^3\mathbf{u}\,\rho_0(\mathbf{u})\,u^2\,. \tag{2.4.35}$$

To get an estimate, let us assume that the charge is distributed uniformly over a sphere of radius u_0. This means that $\rho_0(\mathbf{u})$ is a constant for $u < u_0$

$$\rho_0(\mathbf{u}) \ = \ \frac{3}{4\pi u_0^3}\begin{cases} 1, & u < u_0, \\ 0, & u > u_0\,. \end{cases} \tag{2.4.36}$$

The integral one must evaluate then gives

$$\int d^3\mathbf{u}\,\rho_0(\mathbf{u})u^2 = \int_0^{u_0}\frac{4\pi u^2 du\,u^2}{\frac{4\pi}{3}u_0^3} = \frac{3}{u_0^3}\int_0^{u_0} u^4 du = \tfrac{3}{5}u_0^2\,. \tag{2.4.37}$$

Therefore,

$$\delta V \;=\; \tfrac{1}{10} u_0^2 \, \nabla^2 V \,. \tag{2.4.38}$$

If we choose the radius u_0 of the charge distribution to be the Compton wavelength $\frac{\hbar}{mc}$ of the electron we get,

$$\delta V \;=\; \frac{\hbar^2}{10\, m^2 c^2} \, \nabla^2 V \,. \tag{2.4.39}$$

Comparing with (2.3.14) we see that, up to a small correction ($\frac{1}{8}$ as opposed to $\frac{1}{10}$), this is the Darwin energy shift. The agreement is surprisingly good for what is, admittedly, a heuristic argument.

2.4.2 Relativistic correction

We now turn to the relativistic correction. The energy shifts of the hydrogen states can be analyzed among the degenerate states with principal quantum number n. We write tentatively for the corrections

$$E^{(1)}_{n,\ell m_\ell m_s;\mathrm{rel}} \;=\; -\frac{1}{8m^3c^2} \langle \psi_{n\ell m_\ell m_s} | \mathbf{p}^2 \mathbf{p}^2 | \psi_{n\ell m_\ell} \rangle \,. \tag{2.4.40}$$

We can use this formula because the uncoupled basis of states at fixed n is good: the perturbation is diagonal in this basis. This is checked using Remark 3 in section 1.2.2. This is clear because the perturbing operator $\mathbf{p}^2\mathbf{p}^2$ commutes with $\mathbf{L}^2$, with L_z, and with S_z. The first operator guarantees that that the matrix for the perturbation is diagonal in ℓ, the second guarantees that the perturbation is diagonal in m_ℓ, and the third guarantees, rather trivially, that the perturbation is diagonal in m_s.

To evaluate the matrix element we use the Hermiticity of $\mathbf{p^2}$ to move one of the factors into the bra

$$E^{(1)}_{n,\ell m_\ell m_s;\mathrm{rel}} = -\frac{1}{8m^3c^2} \langle \mathbf{p}^2 \psi_{n\ell m} | \mathbf{p}^2 \psi_{n\ell m} \rangle \,, \tag{2.4.41}$$

where in the right-hand side we evaluated the trivial expectation value for the spin degrees of freedom. To simplify the evaluation we use the Schrödinger equation, which tells us that

$$\Big(\frac{\mathbf{p}^2}{2m} + V \Big) \psi_{n\ell m} \;=\; E^{(0)}_n \psi_{n\ell m} \quad \to \quad \mathbf{p}^2 \psi_{n\ell m} = 2m(E^{(0)}_n - V)\psi_{n\ell m} \,. \tag{2.4.42}$$

Using this both for the bra and the ket:

$$E^{(1)}_{n,\ell m_\ell m_s;\mathrm{rel}} \;=\; -\frac{1}{2mc^2} \, \Big\langle \, (E^{(0)}_n - V)\psi_{n\ell m} \Big| (E^{(0)}_n - V)\psi_{n\ell m} \Big\rangle \,. \tag{2.4.43}$$

The operator $E^{(0)}_n - V$ is also Hermitian and can be moved from the bra to the ket, giving

$$\begin{aligned} E^{(1)}_{n,\ell m_\ell m_s;\mathrm{rel}} &= \; -\frac{1}{2mc^2} \, \Big\langle \psi_{n\ell m} \Big| \big(\, (E^{(0)}_n)^2 - 2V E^{(0)}_n + V^2 \big) \Big| \, \psi_{n\ell m} \Big\rangle \\ &= \; -\frac{1}{2mc^2} \, \Big[(E^{(0)}_n)^2 - 2E_n \langle V \rangle_{n\ell m} + \langle V^2 \rangle_{n\ell m} \Big] \,. \end{aligned} \tag{2.4.44}$$

The problem has been reduced to the computation of the expectation value of $V(r)$ and $V^2(r)$ in the $\psi_{n\ell m}$ state. The expectation value of $V(r)$ is obtained from the virial theorem that states that $\langle V\rangle = 2E_n^{(0)}$. For $V^2(r)$ we have

$$\langle V^2\rangle = e^4\Big\langle\frac{1}{r^2}\Big\rangle = e^4\frac{1}{a_0^2 n^3\left(\ell+\frac{1}{2}\right)} \;=\; \left(\frac{e^2}{2a_0}\frac{1}{n^2}\right)^2\frac{4n}{\ell+\frac{1}{2}} = (E_n^{(0)})^2\cdot\frac{4n}{\ell+\frac{1}{2}}\,. \tag{2.4.45}$$

Back into (2.4.44) we find

$$\boxed{E^{(1)}_{n,\ell m_\ell m_s;\mathrm{rel}} \;=\; -\frac{(E_n^{(0)})^2}{2mc^2}\Big[\,\frac{4n}{\ell+\frac{1}{2}}-3\,\Big] \;=\; -\tfrac{1}{8}\,\alpha^4\frac{(mc^2)}{n^4}\Big[\,\frac{4n}{\ell+\frac{1}{2}}-3\,\Big]\,.} \tag{2.4.46}$$

The complete degeneracy of ℓ multiplets for a given n has been broken. That degeneracy of $H^{(0)}$ was explained by the conserved Runge-Lenz vector. It is clear that the relativistic correction has broken that symmetry.

We have computed the above correction using the uncoupled basis

$$E^{(1)}_{n,\ell m_\ell m_s;\mathrm{rel}} \;=\langle n\ell m m_s|\delta H_{\mathrm{rel}}|n\ell m m_s\rangle \;=\; f(n,\ell)\,. \tag{2.4.47}$$

Here we added the extra equality to emphasize that the matrix elements depend only on n and ℓ. We have already seen that in the full degenerate subspace with principal quantum number n the matrix for δH_{rel} is diagonal in the uncoupled basis. But now we see that in each degenerate subspace of fixed n *and* ℓ, δH_{rel} is in fact a multiple of the *identity* matrix, since the matrix elements are independent of m and m_s (the L_z and S_z) eigenvalues. A matrix equal to a multiple of the identity is invariant under any orthonormal change of basis. For any $\ell\otimes\frac{1}{2}$ multiplet, the resulting j multiplets provide an alternative orthonormal basis. The invariance of a matrix proportional to the identity implies that

$$E^{(1)}_{n\ell j m_j,\mathrm{rel}} = \langle n\ell j m_j|\delta H_{\mathrm{rel}}|n\ell j m_j\rangle \;=\; f(n,\ell)\,. \tag{2.4.48}$$

with the same function $f(n,\ell)$ as in (2.4.47), and the perturbation is diagonal in this coupled basis too. This is clear anyway because the perturbation commutes with $\mathbf{L}^2$, $\mathbf{J^2}$ and J_z and and any two degenerate states in the coupled basis differ either in ℓ, j or j_z.

The preservation of the matrix elements can also be argued more explicitly. Indeed, any state in the coupled basis is a superposition of orthonormal uncoupled basis states with constant coefficients c_i:

$$|n\ell j m_j\rangle \;=\; \sum_i c_i|n\ell m_\ell^i m_s^i\rangle\,,\quad\text{with}\quad \sum_i|c_i|^2=1\,, \tag{2.4.49}$$

because the state on the left-hand side must also have unit norm. Therefore, using the

diagonal nature of the matrix elements in the uncoupled basis we get, as claimed

$$\begin{aligned}\langle n\ell j m_j|\delta H_{\rm rel}|n\ell j m_j\rangle &= \sum_{i,k} c_i^* c_k \langle n\ell m_\ell^i m_s^i|\delta H_{\rm rel}|n\ell m_\ell^k m_s^k\rangle \\ &= \sum_i |c_i|^2 \langle n\ell m_\ell^i m_s^i|\delta H_{\rm rel}|n\ell m_\ell^i m_s^i\rangle \\ &= \sum_i |c_i|^2 f(n,\ell) \;=\; f(n,\ell)\,.\end{aligned} \tag{2.4.50}$$

2.4.3 Spin orbit coupling

The spin-orbit contribution to the Hamiltonian is

$$\delta H_{\text{spin-orbit}} \;=\; \frac{e^2}{2m^2c^2}\frac{1}{r^3}\mathbf{S}\cdot\mathbf{L}\,. \tag{2.4.51}$$

Note that $\delta H_{\text{spin-orbit}}$ commutes with $\mathbf{L}^2$ because $\mathbf{L}^2$ commutes with any $\hat{L}_i$ and any $\hat{S}_i$. Moreover, $\delta H_{\text{spin-orbit}}$ commutes with $\mathbf{J}^2$ and with J_z since, in fact, $[\hat{J}_i\,,\,\mathbf{S}\cdot\mathbf{L}] = 0$ for any i; $\mathbf{S}\cdot\mathbf{L}$ is a scalar operator for $\mathbf{J}$. It follows that $\delta H_{\text{spin-orbit}}$ is diagonal in the level n degenerate subspace in the coupled basis $|n\ell j m_j\rangle$. In fact, as we will see, the matrix elements are m-independent. This is a nontrivial consequence of $\delta H_{\text{spin-orbit}}$ being a scalar under $\mathbf{J}$. To compute the matrix elements we recall that $\mathbf{J} = \mathbf{S} + \mathbf{L}$ and

$$\begin{aligned}E^{(1)}_{n\ell j m_j;\,\text{spin-orbit}} &= \frac{e^2}{2m^2c^2}\left\langle n\ell j m_j\middle|\frac{1}{r^3}\mathbf{S}\cdot\mathbf{L}\middle|n\ell j m_j\right\rangle \\ &= \frac{e^2}{2m^2c^2}\frac{\hbar^2}{2}\left[j(j+1)-\ell(\ell+1)-\tfrac{3}{4}\right]\left\langle n\ell j m_j\middle|\frac{1}{r^3}\middle|n\ell j m_j\right\rangle.\end{aligned} \tag{2.4.52}$$

We need the expectation value of $1/r^3$ in these states. It is known that

$$\left\langle n\ell m_\ell\middle|\frac{1}{r^3}\middle|n\ell m_\ell\right\rangle \;=\; \frac{1}{n^3a_0^3\ell\left(\ell+\frac{1}{2}\right)(\ell+1)}\,. \tag{2.4.53}$$

Because of the m_ℓ independence of this expectation value (and its obvious m_s independence) the operator $1/r^3$ is a multiple of the identity matrix in each $\ell\otimes\frac{1}{2}$ multiplet. It follows that it is the same multiple of the identity in the coupled basis description. Therefore

$$\left\langle n\ell j m_j\middle|\frac{1}{r^3}\middle|n\ell j m_j\right\rangle \;=\; \frac{1}{n^3a_0^3\ell\left(\ell+\frac{1}{2}\right)(\ell+1)}\,. \tag{2.4.54}$$

Using this in (2.4.52)

$$E^{(1)}_{n\ell j m_j;\,\text{spin-orbit}} = \frac{e^2\hbar^2}{4m^2c^2}\frac{\left[j(j+1)-\ell(\ell+1)-\frac{3}{4}\right]}{n^3a_0^3\ell\left(\ell+\frac{1}{2}\right)(\ell+1)}\,. \tag{2.4.55}$$

Working out the constants in terms of $E_n^{(0)}$ and rest energies we get

$$E^{(1)}_{n\ell j m_j;\,\text{spin-orbit}} \;=\; \frac{(E_n^{(0)})^2}{mc^2}\,\frac{n\left[j(j+1)-\ell(\ell+1)-\frac{3}{4}\right]}{\ell\left(\ell+\frac{1}{2}\right)(\ell+1)}\,, \qquad \ell\neq 0\,. \tag{2.4.56}$$

Since $\mathbf{L}$ vanishes identically acting on any $\ell = 0$ state, it is physically reasonable, as we will do, to assume that the spin-orbit correction vanishes for $\ell = 0$ states. On the other hand the limit of the above formula as $\ell \to 0$, while somewhat ambiguous, is nonzero. We set $j = \ell + \frac{1}{2}$ (the other possibility $j = \ell - \frac{1}{2}$ does not apply for $\ell = 0$) and then take the limit as $\ell \to 0$. Indeed,

$$\begin{aligned} E^{(1)}_{n\ell j m_j;\,\text{spin-orbit}}\Big|_{j=\ell+\frac{1}{2}} &= \frac{(E_n^{(0)})^2}{mc^2}\,\frac{n\left[(\ell+\frac{1}{2})(\ell+\frac{3}{2})-\ell(\ell+1)-\frac{3}{4}\right]}{\ell\left(\ell+\frac{1}{2}\right)(\ell+1)} \\ &= \frac{(E_n^{(0)})^2}{mc^2}\,\frac{n}{\left(\ell+\frac{1}{2}\right)(\ell+1)}\,, \end{aligned} \tag{2.4.57}$$

and now taking the limit:

$$\lim_{\ell\to 0} E^{(1)}_{n\ell j m_j;\,\text{spin-orbit}}\Big|_{j=\ell+\frac{1}{2}} = \frac{(E_n^{(0)})^2}{mc^2}(2n) \;=\; \alpha^4\, mc^2\,\frac{1}{2n^3}\,. \tag{2.4.58}$$

We see that this limit is in fact identical to the Darwin shift (2.4.24) of the nS states. This is a bit surprising and will play a technical role below.

2.4.4 Combining results

For $\ell \neq 0$ states we can add the energy shifts from spin-orbit and from the relativistic correction, both of them expressed as expectation values in the coupled basis. The result, therefore will give the shifts of the coupled states. Collecting our results (2.4.46) and (2.4.56) we have

$$\begin{aligned} &\left\langle n\ell j m_j\middle|\delta H_{\text{rel}} + \delta H_{\text{spin-orbit}}\middle|n\ell j m_j\right\rangle \\ &\qquad = \frac{(E_n^{(0)})^2}{2mc^2}\left\{3 - \frac{4n}{\left(\ell+\frac{1}{2}\right)} + \frac{2n\left[j(j+1)-\ell(\ell+1)-\frac{3}{4}\right]}{\ell\left(\ell+\frac{1}{2}\right)(\ell+1)}\right\} \\ &\qquad = \frac{(E_n^{(0)})^2}{2mc^2}\left\{3 + 2n\left[\frac{j(j+1)-3\ell(\ell+1)-\frac{3}{4}}{\ell\left(\ell+\frac{1}{2}\right)(\ell+1)}\right]\right\}. \end{aligned} \tag{2.4.59}$$

These are the fine structure energy shifts for all states in the spectrum of hydrogen. The states in a coupled multiplet are characterized by ℓ, j and m_j and each multiplet as a whole is shifted according to the above formula. The degeneracy within the multiplet is unbroken because the formula has no m_j dependence. This formula, as written, hides some additional degeneracies. We uncover those next.

In the above formula there are two cases to consider for any *fixed* value of j: the multiplet can have $\ell = j - \frac{1}{2}$ or the multiplet can have $\ell = j + \frac{1}{2}$. We will now see something rather surprising. In both of these cases the shift is the same, meaning that the shift is in fact ℓ independent! It just depends on j. Call $f(j,\ell)$ the term in brackets above

$$f(j,\ell) \;\equiv\; \frac{j(j+1) - 3\ell(\ell+1) - \frac{3}{4}}{\ell\left(\ell+\frac{1}{2}\right)(\ell+1)}\,. \tag{2.4.60}$$

The evaluation of this expression in both cases gives the same result:

$$\begin{aligned} f(j,\ell)\Big|_{\ell=j-\frac{1}{2}} &= \frac{j(j+1) - 3(j-\frac{1}{2})(j+\frac{1}{2}) - \frac{3}{4}}{\left(j-\frac{1}{2}\right) j \left(j+\frac{1}{2}\right)} = \frac{-2j^2 + j}{j\left(j-\frac{1}{2}\right)\left(j+\frac{1}{2}\right)} = -\frac{2}{\left(j+\frac{1}{2}\right)}\,, \\ f(j,\ell)\Big|_{\ell=j+\frac{1}{2}} &= \frac{j(j+1) - 3(j+\frac{1}{2})(j+\frac{3}{2}) - \frac{3}{4}}{\left(j+\frac{1}{2}\right)(j+1)\left(j+\frac{3}{2}\right)} = \frac{2j^2 - 5j - 3}{\left(j+\frac{1}{2}\right)(j+1)\left(j+\frac{3}{2}\right)} = -\frac{2}{\left(j+\frac{1}{2}\right)}\,. \end{aligned} \tag{2.4.61}$$

We can therefore replace in (2.4.59) the result of our evaluation, which we label as fine structure (fs) shifts:

$$E^{(1)}_{n\ell j,m_j;\text{fs}} \;=\; -\frac{(E^{(0)}_n)^2}{2mc^2}\Big[\;\frac{4n}{j+\frac{1}{2}} - 3\;\Big] \;=\; -\alpha^4(mc^2)\frac{1}{2n^4}\Big[\;\frac{n}{j+\frac{1}{2}} - \tfrac{3}{4}\;\Big]\,. \tag{2.4.62}$$

More briefly we can write

$$\boxed{E^{(1)}_{n\ell j,m_j;\text{fine}} \;=\; -\alpha^4 mc^2 \cdot S_{n,j}\,, \quad \text{with} \quad S_{n,j} \;\equiv\; \frac{1}{2n^4}\Big[\;\frac{n}{j+\frac{1}{2}} - \tfrac{3}{4}\;\Big]\,.} \tag{2.4.63}$$

Let us consider a few remarks:

1. The dependence on j and absence of dependence on ℓ in the energy shifts could be anticipated from the Dirac equation. The rotation generator that commutes with the Dirac Hamiltonian is $\mathbf{J} = \mathbf{L} + \mathbf{S}$, which simultaneously rotates position, momenta, and spin states. Neither $\mathbf{L}$ nor $\mathbf{S}$ are separately conserved. With $\mathbf{J}$ a symmetry, states are expected to be labelled by energy and j and must be m_j independent.

2. The formula (2.4.63) works for nS states! For these $\ell = 0$ states we were supposed to add the relativistic correction and the Darwin correction, since their spin-orbit correction is zero. But we noticed that the limit $\ell \to 0$ of the spin-orbit correction reproduces the Darwin term. Whether or not this is a meaningful coincidence, it means the sum performed above gives the right answer for $\ell \to 0$.

3. While a large amount of the degeneracy of $H^{(0)}$ has been broken, for fixed n, multiplets with the same value of j, regardless of ℓ, remain degenerate. The states in each j multiplet do not split.

4. Since $S_{n,j} > 0$ all energy shifts are down. Indeed

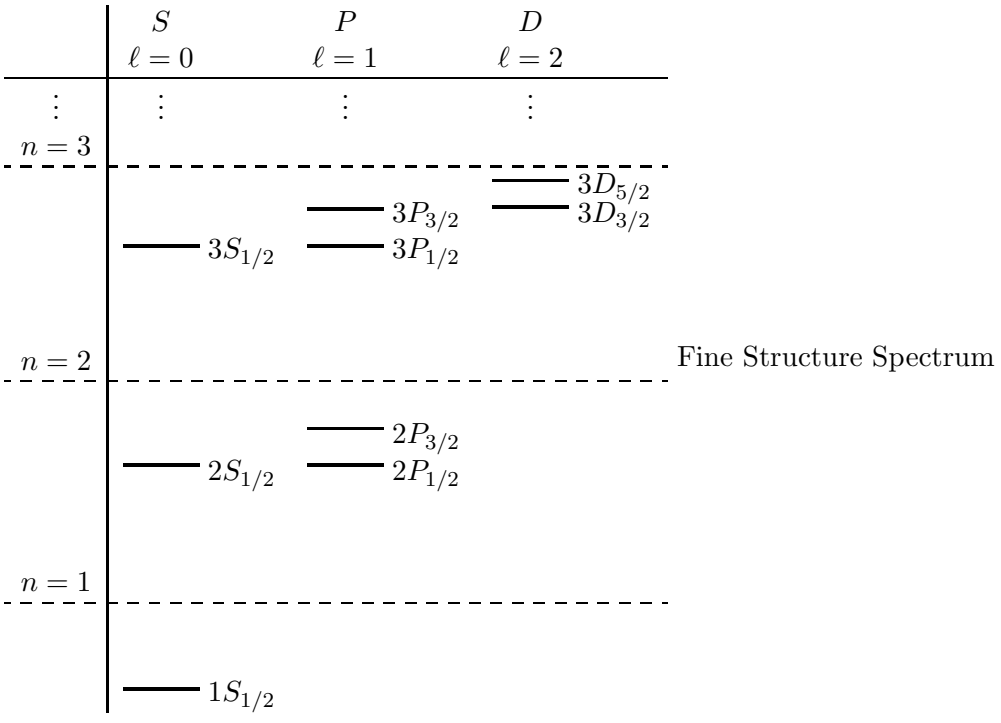
$$\frac{n}{j+\frac{1}{2}} \geq \frac{n}{j_{\max}+\frac{1}{2}} = \frac{n}{\ell_{\max}+\frac{1}{2}+\frac{1}{2}} = \frac{n}{n} = 1 \quad \rightarrow \quad \frac{n}{j+\frac{1}{2}} - \tfrac{3}{4} \geq \tfrac{1}{4}\,. \tag{2.4.64}$$

5. For a given fixed n, states with lower values of j get pushed further down. As n increases splittings fall off like n^{-3}.

A table of values of $S_{n,j}$ is given here below

n	j	$S_{n,j}$
1	$\frac{1}{2}$	$\frac{1}{8}$
2	$\frac{1}{2}$	$\frac{5}{128}$
	$\frac{3}{2}$	$\frac{1}{128}$
3	$\frac{1}{2}$	$\frac{1}{72}$
	$\frac{3}{2}$	$\frac{1}{216}$
	$\frac{5}{2}$	$\frac{1}{648}$

The energy diagram for states up to $n = 3$ is given here (not to scale)



For the record, the total energy of the hydrogen states is the zeroth contribution plus the fine structure contribution. Together they give

$$E_{n\ell jm_j} = -\frac{e^2}{2a_0}\frac{1}{n^2}\Big[1+\frac{\alpha^2}{n^2}\Big(\frac{n}{j+\frac{1}{2}}-\tfrac{3}{4}\Big)\Big]\,. \tag{2.4.65}$$

This is the fine structure of hydrogen! There are, of course, finer corrections. The so-called Lamb shift, for example, breaks the degeneracy between $2S_{1/2}$ and $2P_{1/2}$ and is of order α^5. There is also hyperfine splitting, which arises from the coupling of the magnetic moment of the proton to the magnetic moment of the electron. Such coupling leads to a splitting that is a factor m_e/m_p smaller than fine structure.

2.5 Zeeman effect

In remarkable experiment done in 1896, the Dutch physicist Pieter Zeeman (1865-1943) discovered that atomic spectral lines are split in the presence of an external magnetic field. For this work Zeeman was awarded the Nobel Prize in 1902. The proper understanding of this phenomenon had to wait for Quantum Mechanics.

The splitting of atomic energy levels by a constant, uniform, external magnetic field, the *Zeeman effect*, has been used as a tool to measure inaccessible magnetic fields. In observing the solar spectrum, a single atomic line, as seen from light emerging from outside a sunspot, splits into various lines inside the sunspot. We have learned that magnetic fields inside a sunspot typically reach $3,000$ gauss. Sunspots are a bit darker and have lower temperature than the rest of the solar surface. They can last from hours to months, and their magnetic energy can turn into powerful solar flares.

The external magnetic field interacts with the total magnetic moment of the electron. The electron has magnetic moment due to its orbital angular momentum and one due to its spin

$$\boldsymbol{\mu}_\ell \;=\; -\frac{e}{2mc}\,\mathbf{L}\,, \quad \boldsymbol{\mu}_s \;=\; -\frac{e}{mc}\,\mathbf{S}\,, \tag{2.5.1}$$

where we included the $g=2$ factor in the spin contribution. The Zeeman Hamiltonian is thus given by

$$\delta H_{\text{Zeeman}} \;=\; -(\boldsymbol{\mu}_\ell+\boldsymbol{\mu}_s)\cdot\mathbf{B} \;=\; \frac{e}{2mc}\,(\mathbf{L}+2\mathbf{S})\cdot\mathbf{B}\,. \tag{2.5.2}$$

Conventionally, we align the magnetic field with the positive z axis so that $\mathbf{B}=B\,\mathbf{z}$ and thus get

$$\delta H_{\text{Zeeman}} \;=\; \frac{eB}{2mc}\,(\hat{L}_z+2\hat{S}_z)\,. \tag{2.5.3}$$

When we consider the Zeeman effect on Hydrogen we must not forget fine structure. The full Hamiltonian to be considered is

$$H \;=\; H^{(0)}+\delta H_{\text{fs}}+\delta H_{\text{Zeeman}}\,. \tag{2.5.4}$$

Recall that in fine structure, there is an internal magnetic field $B_{\rm int}$ associated with spin-orbit coupling. This is the magnetic field seen by the electron as it goes around the proton. We have therefore two extreme possibilities concerning the external magnetic field B of the Zeeman effect:

(1) Weak-field Zeeman effect: $B \ll B_{\rm int}$. In this case the Zeeman effect is small compared with fine structure effects. Accordingly, the original Hamiltonian $H^{(0)}$ *together* with the fine structure Hamiltonian $H_{\rm fs}$ are thought as the "known" Hamiltonian $\tilde{H}^{(0)}$, and the Zeeman Hamiltonian is the perturbation:

$$H \;=\; \underbrace{H^{(0)} + \delta H_{\rm fs}}_{\tilde{H}^{(0)}} + \delta H_{\rm Zeeman}\,. \tag{2.5.5}$$

(2) Strong-field Zeeman effect: $B \gg B_{\rm int}$. In this case the Zeeman effect is much larger than fine structure effects. Accordingly, the original Hamiltonian $H^{(0)}$ *together* with the Zeeman Hamiltonian are thought as the "known" Hamiltonian $\check{H}^{(0)}$ and the fine structure Hamiltonian $H_{\rm fs}$ is viewed as the perturbation:

$$H \;=\; \underbrace{H^{(0)} + \delta H_{\rm Zeeman}}_{\check{H}^{(0)}} + \delta H_{\rm fs}\,. \tag{2.5.6}$$

You may thing that $H^{(0)} + \delta H_{\rm Zeeman}$ does not qualify as known, but happily, as we will confirm soon, this is actually a very simple Hamiltonian.

When the Zeeman magnetic field is neither weak nor strong, we must take the sum of the Zeeman and fine structure Hamiltonians as the perturbation. No simplification is possible and one must diagonalize the perturbation.

Weak-field Zeeman effect. The approximate eigenstates of $\tilde{H}^{(0)}$ are the coupled states $|n\ell j m_j\rangle$ that exhibit fine structure corrections and whose energies are a function of n and j, as shown in the Fine Structure diagram. Degeneracies in this spectrum occur for different values of ℓ and different values of m_j.

To figure out the effect of the Zeeman interaction on this spectrum we consider the matrix elements:

$$\langle n\ell j m_j|\delta H_{\rm Zeeman}|n\ell' j m_j'\rangle\,. \tag{2.5.7}$$

Since $\delta H_{\rm Zeeman} \sim L_z + 2S_z$ we see that $\delta H_{\rm Zeeman}$ commutes with $\mathbf{L^2}$ and with $\hat{J}_z$. The matrix element thus vanishes unless $\ell' = \ell$ and $m_j' = m_j$ and the Zeeman perturbation is diagonal in the degenerate fine structure eigenspaces. The energy corrections are therefore

$$E^{(1)}_{n\ell j m_j} \;=\; \frac{e\hbar}{2mc}\,B\,\langle n\ell j m_j|(\hat{L}_z + 2\hat{S}_z)|n\ell j m_j\rangle\frac{1}{\hbar}\,, \tag{2.5.8}$$

where we multiplied and divided by $\hbar$ to make the units of the result manifest. The result of the evaluation of the matrix element will show a remarkable feature: a linear dependence

$E^{(1)} \sim \hbar m_j$ on the azimuthal quantum numbers. The states in each j multiplet split into equally separated energy levels! We will try to understand this result as a property of matrix elements of vector operators. First, however, note that $\hat{L}_z + 2\hat{S}_z = \hat{J}_z + \hat{S}_z$ and therefore the matrix element of interest in the above equation satisfies

$$\langle n\ell j m_j | (\hat{L}_z + 2\hat{S}_z) | n\ell j m_j \rangle \;=\; \hbar m + \langle n\ell j m_j | \hat{S}_z | n\ell j m_j \rangle \,. \tag{2.5.9}$$

It follows that we only need to concern ourselves with $\hat{S}_z$ matrix elements.

Let's talk about vector operators. The operator $\hat{\mathbf{V}}$ is said to be a vector operator under an angular momentum operator $\hat{\mathbf{J}}$ if the following commutator holds for all values of $i, j = 1, 2, 3$:

$$\big[\, \hat{J}_i \,,\, \hat{V}_j \,\big] \;=\; i\hbar\, \epsilon_{ijk}\, \hat{V}_k \,. \tag{2.5.10}$$

It follows from the familiar $\hat{\mathbf{J}}$ commutators that $\hat{\mathbf{J}}$ is a vector operator under $\hat{\mathbf{J}}$. Additionally, if $\hat{\mathbf{V}}$ is a vector operator it has a standard commutation relation with $\hat{\mathbf{J}}^2$ that can be quickly confirmed:

$$[\hat{\mathbf{J}}^2 \,, \hat{\mathbf{V}}] \;=\; 2i\hbar \left(\hat{\mathbf{V}} \times \hat{\mathbf{J}} \;- i\hbar\, \hat{\mathbf{V}} \right). \tag{2.5.11}$$

If $\hat{\mathbf{V}}$ is chosen to be $\hat{\mathbf{J}}$ the left-hand side vanishes by the standard property of $\hat{\mathbf{J}}^2$ and the right-hand side vanishes because the $\hat{\mathbf{J}}$ commutation relations can be written as $\hat{\mathbf{J}} \times \hat{\mathbf{J}} = i\hbar \hat{\mathbf{J}}$. Finally, by repeated use of the above identities you will show (homework) that the following formula holds

$$\frac{1}{(2i\hbar)^2} \Big[\hat{\mathbf{J}}^2 \,, [\hat{\mathbf{J}}^2 \,, \hat{\mathbf{V}}] \Big] \;=\; (\hat{\mathbf{V}} \cdot \hat{\mathbf{J}})\, \hat{\mathbf{J}} \;-\; \tfrac{1}{2} \left(\hat{\mathbf{J}^2}\, \hat{\mathbf{V}} + \hat{\mathbf{V}}\, \hat{\mathbf{J}^2} \right). \tag{2.5.12}$$

Consider $(\hat{\mathbf{J}}^2, \hat{J}_z)$ eigenstates $|k;\, j m_j\rangle$ where k stands for other quantum number that bear no relation to angular momentum. The matrix elements of the left-hand side of (2.5.12) on such eigenstates is necessarily zero:

$$\langle k';\, j m_j' | \Big[\hat{\mathbf{J}}^2 \,, [\hat{\mathbf{J}}^2 \,, \hat{\mathbf{V}}] \Big] | k;\, j m_j \rangle \;=\; 0 \,, \tag{2.5.13}$$

as can be seen by expanding the outer commutator and noticing that $\hat{\mathbf{J}}^2$ gives the same eigenvalue when acting on the bra and on the ket. Therefore the matrix elements of the right-hand side gives

$$\langle k';\, j m_j' | (\hat{\mathbf{V}} \cdot \hat{\mathbf{J}})\, \hat{\mathbf{J}} | k;\, j m_j \rangle \;=\; \hbar^2\, j(j+1)\, \langle k';\, j m_j' | \hat{\mathbf{V}} | k;\, j m_j \rangle \,, \tag{2.5.14}$$

which implies that

$$\boxed{\langle k';\, j m_j' | \hat{\mathbf{V}} | k;\, j m_j \rangle \;=\; \frac{\langle k';\, j m_j' | (\hat{\mathbf{V}} \cdot \hat{\mathbf{J}})\, \hat{\mathbf{J}} | k;\, j m_j \rangle}{\hbar^2\, j(j+1)} \,.} \tag{2.5.15}$$

This is the main identity we wanted to establish. Using the less explicit notation $\langle \cdots \rangle$ for the matrix elements we have found that

$$\langle \hat{\mathbf{V}} \rangle \;=\; \frac{\langle (\hat{\mathbf{V}} \cdot \hat{\mathbf{J}})\, \hat{\mathbf{J}} \,\rangle}{\langle \hat{\mathbf{J}}^2 \rangle} \,. \tag{2.5.16}$$

This is sometimes called the projection lemma: the matrix elements of a vector operator $\hat{\mathbf{V}}$ are those of the conventional projection of $\hat{\mathbf{V}}$ onto $\hat{\mathbf{J}}$. Recall that the projection of a vector $\mathbf{v}$ along the vector $\mathbf{j}$ is $(\mathbf{v}\cdot\mathbf{j})\mathbf{j}/\mathbf{j}^2$.

Let us now return to the question of interest; the computation of the the expectation value of $\hat{S}_z$ in (2.5.20). Since $\hat{\mathbf{S}}$ is a vector operator under $\hat{\mathbf{J}}$ we can use (2.5.15). Specializing to the z-component

$$\langle n\ell\, jm_j|\hat{S}_z|n\ell\, jm_j\rangle \;=\; \frac{\hbar m_j\,\langle n\ell\, jm_j|\hat{\mathbf{S}}\cdot\hat{\mathbf{J}}\,|n\ell\, jm_j\rangle}{\hbar^2\, j(j+1)}\,. \tag{2.5.17}$$

We already see the appearance of the predicted $\hbar m_j$ factor. The matrix element in the numerator is still to be calculated but it will introduce no m_j dependence. In fact $\hat{\mathbf{S}}\cdot\hat{\mathbf{J}}$ is a scalar operator (it commutes with all $\hat{J}_i$) and therefore it is diagonal in m_j. But even more is true; the expectation value of a scalar operator is in fact independent of m_j! We will not show this here, but will just confirm it by direct computation. Since $\hat{\mathbf{L}}=\hat{\mathbf{J}}-\hat{\mathbf{S}}$ we have

$$\hat{\mathbf{S}}\cdot\hat{\mathbf{J}} \;=\; \tfrac{1}{2}\big(\hat{\mathbf{J}}^2+\hat{\mathbf{S}}^2-\hat{\mathbf{L}}^2\big)\,, \tag{2.5.18}$$

and therefore

$$\langle n\ell\, jm_j|\hat{S}_z|n\ell\, jm_j\rangle \;=\; \frac{\hbar m_j}{2j(j+1)}\,\big(j(j+1)-\ell(\ell+1)+\tfrac{3}{4}\big)\,. \tag{2.5.19}$$

Indeed, no further m_j dependence has appeared. Back now to (2.5.20) we get

$$\langle n\ell jm_j|(\hat{L}_z+2\hat{S}_z)|n\ell jm_j\rangle \;=\; \hbar m_j\Big(1+\frac{j(j+1)-\ell(\ell+1)+\frac{3}{4}}{2j(j+1)}\Big)\,. \tag{2.5.20}$$

The constant of proportionality in parenthesis is called the **Lande g-factor** $g_J(\ell)$:

$$g_J(\ell) \;\equiv\; 1+\frac{j(j+1)-\ell(\ell+1)+\frac{3}{4}}{2j(j+1)} \tag{2.5.21}$$

We finally have for the Zeeman energy shifts in (2.5.8)

$$E^{(1)}_{n\ell jm_j} \;=\; \frac{e\hbar}{2mc}\,B\,g_J(\ell)\,m_j\,. \tag{2.5.22}$$

Here the Bohr magneton $\frac{e\hbar}{2mc}\simeq 5.79\times10^{-9}$eV/gauss. This is our final result for the weak-field Zeeman energy corrections to the fine structure energy levels. Since all degeneracies within j multiplets are broken and j multiplets with different ℓ split differently due to the ℓ dependence of $g_J(\ell)$, the weak-field Zeeman effect removes all degeneracies!

Strong-field Zeeman effect. We mentioned earlier that when the Zeeman effect is larger than the fine structure corrections we must take the original hydrogen Hamiltonian together with the Zeeman Hamiltonian to form the 'known' Hamiltonian $\check{H}^{(0)}$:

$$\check{H}^{(0)} \;=\; H^{(0)}+\frac{e}{2mc}\,(\hat{L}_z+2\hat{S}_z)B\,. \tag{2.5.23}$$

Actually $\check{H}^{(0)}$ is simple because the Zeeman Hamiltonian commutes with the zero-th order hydrogen Hamiltonian

$$\left[\,\hat{L}_z + 2\hat{S}_z\,,\,H^{(0)}\right] \;=\; 0\,. \tag{2.5.24}$$

We can thus find eigenstates of both simultaneously. Those are in fact the uncoupled basis states! We have

$$\begin{aligned} H^{(0)}|n\ell m_\ell m_s\rangle &= E_n^{(0)}|n\ell m_\ell m_s\rangle \\ (\hat{L}_z + 2\hat{S}_z)|n\ell m_\ell m_s\rangle &= \hbar(m_\ell + 2m_s)|n\ell m_\ell m_s\rangle\,. \end{aligned} \tag{2.5.25}$$

and therefore the uncoupled basis states are the *exact* energy eigenstates of $\check{H}^{(0)}$ and have energies

$$E_{n\ell m_\ell m_s} \;=\; E_n^{(0)} + \frac{e\hbar}{2mc}B(m_\ell + 2m_s)\,. \tag{2.5.26}$$

Some of the degeneracy of $H^{(0)}$ has been removed, but some remains. For a fixed principal quantum number n there are degeneracies among $\ell \otimes \frac{1}{2}$ states and degeneracies among such multiplets with ℓ and ℓ' different. This is illustrated in Figure 2.2.

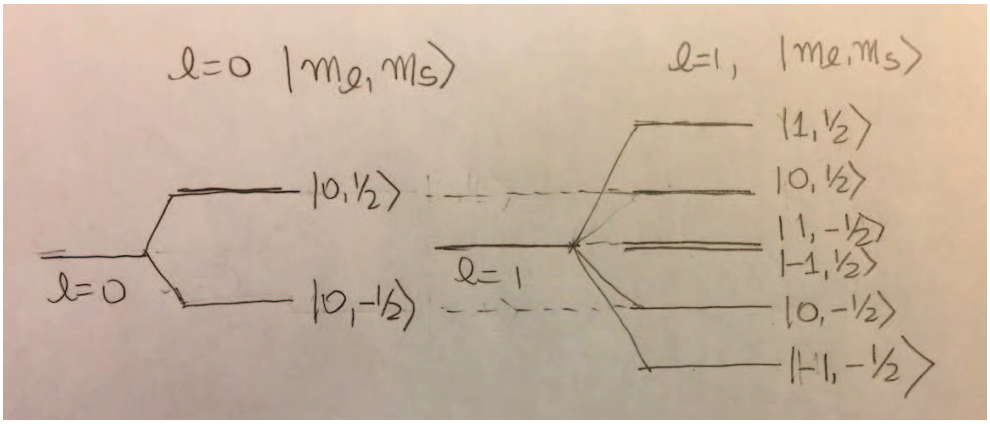


Figure 2.2: Illustrating the degeneracies remaining for $\ell = 0$ and $\ell = 1$ after the inclusion of Zeeman term in the Hamiltonian. Accounting for the spin of the electron there two degenerate states in the $\ell = 1$ multiplet $1 \otimes \frac{1}{2}$ and each of the two states in the $\ell = 0$ multiplet $0 \otimes \frac{1}{2}$ is degenerate with a state in the $\ell = 1$ multiplet.

The problem now is to compute the corrections due to $\delta H_{\rm fs}$ on the non-degenerate and on the degenerate subspaces of $\check{H}^{(0)}$. The non-degenerate cases are straightforward, but the degenerate cases could involve diagonalization. We must therefore consider the matrix elements

$$\langle n\ell' m'_\ell m'_s|\,\delta H_{\rm fs}|n\ell m_\ell m_s\rangle\,, \tag{2.5.27}$$

with the condition

$$m'_\ell + 2m'_s \;=\; m_\ell + 2m_s\,, \tag{2.5.28}$$

needed for the two states in the matrix element to belong to a degenerate subspace. Since $\hat{\mathbf{L}}^2$ commutes with $\delta H_{\rm fs}$ the matrix elements vanish unless $\ell = \ell'$ and therefore it suffices to consider the matrix elements

$$\langle n\ell' m'_\ell m'_s|\, \delta H_{\rm fs} | n\ell m_\ell m_s\rangle\,, \tag{2.5.29}$$

still with condition (2.5.28). Ignoring $\ell = 0$ states, we have to re-examine the relativistic correction and spin orbit. The relativistic correction was computed in the uncoupled basis and one can use the result because the states are unchanged and the perturbation was shown to be diagonal in this basis. For spin-orbit the calculation was done in the coupled basis because spin-orbit is *not diagonal* in the original $H^{(0)}$ degenerate spaces using the uncoupled basis. But happily, it turns out that spin-orbit is diagonal in the more limited degenerate subspaces obtained after the Zeeman effect is included. All these matters are explored in the homework.

Chapter 3

Semiclassical approximation

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3.1 The classical limit

The WKB approximation provides approximate solutions for linear differential equations with coefficients that have slow spatial variation. The acronym WKB stands for Wentzel, Kramers, Brillouin, who independently discovered it in 1926. It was in fact discovered earlier, in 1923 by the mathematician Jeffreys. When applied to quantum mechanics, it is called the *semi-classical* approximation, since classical physics then illuminates the main features of the *quantum* wavefunction.

The de Broglie wavelength λ of a particle can help us assess if classical physics is relevant to the physical situation. For a particle with momentum p we have

$$\lambda = \frac{h}{p}\,. \tag{3.1.1}$$

Classical physics provides useful physical insight when λ is much smaller than the relevant length scale in the problem we are investigating. Alternatively if we take $h \to 0$ this will formally make $\lambda \to 0$, or λ smaller than the length scale of the problem. Being a constant of nature, we cannot really make $\hbar \to 0$, so taking this limit is a thought experiment in which we imagine worlds in which h takes smaller and smaller values making classical physics more and more applicable. The semi-classical approximation studied here will be applicable if a suitable generalization of the de Broglie wavelength discussed below is small and slowly varying. The semi-classical approximation will be set up mathematically by thinking of $\hbar$ as a parameter that can be taken to be as small as desired.

Our discussion in this chapter will focus on one-dimensional problems. Consider therefore a particle of mass m and total energy E moving in a potential $V(x)$. In classical physics $E - V(x)$ is the kinetic energy of the particle at x. This kinetic energy depends on position.

Since kinetic energy is $\frac{p^2}{2m}$ this suggests the definition of the **local momentum** $p(x)$:

$$p^2(x) \;\equiv\; 2m(E - V(x))\,. \tag{3.1.2}$$

The local momentum $p(x)$ is the momentum of the classical particle when it is located at x. With a notion of local momentum, we can define a **local de Broglie wavelength** $\lambda(x)$ by the familiar relation:

$$\boxed{\lambda(x) \equiv \frac{h}{p(x)} = \frac{2\pi\hbar}{p(x)}\,.} \tag{3.1.3}$$

The time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) \;=\; (E - V(x))\psi(x)\,. \tag{3.1.4}$$

can be written nicely in terms of the local momentum squared :

$$-\hbar^2\frac{\partial^2}{\partial x^2}\psi \;=\; p^2(x)\,\psi\,. \tag{3.1.5}$$

Using the momentum operator, this equation takes the suggestive form

$$\boxed{\hat{p}^2\,\psi(x) \;=\; p^2(x)\,\psi(x)\,.} \tag{3.1.6}$$

This has the flavor of an eigenvalue equation but it is not one: the action of the momentum operator squared on the wavefunction is not really proportional to the wavefunction, it is the wavefunction multiplied by the 'classical' position-dependent momentum-squared.

A bit of extra notation is useful. If we are in the classically allowed region, $E > V(x)$ and $p^2(x)$ is positive. We then write

$$p^2(x) \;=\; 2m(E - V(x)) = \;\hbar^2k^2(x)\,, \tag{3.1.7}$$

introducing the local, real wavenumber $k(x)$. If we are in the classically forbidden region, $V(x) > E$ and $p^2(x)$ is negative. We then write

$$-p^2(x) \;=\; 2m(V(x) - E) = \;\hbar^2\kappa^2(x)\,, \tag{3.1.8}$$

introducing the local, real $\kappa(x)$.

The wavefunctions we use in the WKB approximation are often expressed in polar form. Just like any complex number z can be written as $re^{i\theta}$, where r and θ are the magnitude and phase of z, respectively, we can write the wavefunction in a similar way:

$$\Psi(\mathbf{x},t) = \sqrt{\rho(\mathbf{x},t)}\;\exp\Big(\frac{i}{\hbar}\mathcal{S}(\mathbf{x},t)\Big)\,. \tag{3.1.9}$$

We are using here three-dimensional notation for generality. By definition, the functions $\rho(\mathbf{x},t)$ and $\mathcal{S}(\mathbf{x},t)$ are real. The function ρ is non-negative and the function $\mathcal{S}(\mathbf{x},t)$ as written, has units of $\hbar$. The name $\rho(\mathbf{x},t)$ is well motivated, for it is in fact the probability density:

$$\rho(\mathbf{x},t) \;=\; |\Psi(\mathbf{x},t)|^2\,. \tag{3.1.10}$$

Let's compute the probability current. For this we begin by taking the gradient of the wavefunction

$$\nabla\Psi = \frac{1}{2}\frac{\nabla\rho}{\sqrt{\rho}}e^{\frac{i\mathcal{S}}{\hbar}} + \frac{i}{\hbar}\nabla\mathcal{S}\,\Psi \tag{3.1.11}$$

We then form:

$$\Psi^*\nabla\Psi = \frac{1}{2}\nabla\rho + \frac{i}{\hbar}\rho\nabla\mathcal{S} \tag{3.1.12}$$

The current is given by

$$\mathbf{J} = \frac{\hbar}{m}\,\mathrm{Im}\,(\Psi^*\nabla\Psi)\;. \tag{3.1.13}$$

It follows that

$$\boxed{\mathbf{J} \;=\; \rho\frac{\nabla\mathcal{S}}{m}\,.} \tag{3.1.14}$$

This formula implies that the probability current $\mathbf{J}$ is perpendicular to the surfaces of constant $\mathcal{S}$, the surfaces of constant phase in the wavefunction.

In classical physics a fluid with density $\rho(\mathbf{x})$ moving with velocity $\mathbf{v}(\mathbf{x})$ has a current density $\rho\mathbf{v} = \rho\frac{\mathbf{p}}{m}$. Comparing with the above expression for the quantum probability current, we deduce that

$$\mathbf{p}(\mathbf{x}) \;\simeq\; \nabla\mathcal{S}\,. \tag{3.1.15}$$

We use the $\simeq$ because this is an association that is not of general validity. Nevertheless, for 'basic' WKB solutions we will see that the gradient of $\mathcal{S}$ is indeed the classical local momentum! This association also holds for a free particle:

Example. Consider a free particle with momentum $\mathbf{p}$ and energy E. Its wavefunction is

$$\Psi(\mathbf{x},t) = \exp\left[\;\frac{i\mathbf{p}\cdot\mathbf{x}}{\hbar} - \frac{iEt}{\hbar}\;\right]. \tag{3.1.16}$$

Here we identify the function $\mathcal{S}$ as $\mathcal{S} = \mathbf{p}\cdot\mathbf{x} - Et$ and therefore $\nabla\mathcal{S} = \mathbf{p}$. In this case $\nabla\mathcal{S}$ is equal to the momentum eigenvalue, a constant.

3.2 WKB approximation scheme

Our aim here is to find approximate solutions for the wavefunction $\psi(x)$ that solves the time independent Schrödinger equation in one dimension. We wrote before the polar decomposition (3.1.9) of the wavefunction. It will be easier to set the approximation scheme by

using a single complex function $S(x)$ to represent the time-independent wavefunction $\psi(x)$. For this we use a *pure* exponential without any prefactor:

$$\psi(x) = \exp\Big(\frac{i}{\hbar}S(x)\Big)\,, \quad S(x) \in \mathbb{C}\,. \tag{3.2.1}$$

As before S must have units of $\hbar$. This $S(x)$ here is a *complex* number, because wavefunctions are not in general pure phases. The real part of S, divided by $\hbar$, is the phase of the wavefunction. The imaginary part of $S(x)$ determines the magnitude of the wavefunction.

Let us plug this into the Schrödinger equation (3.1.5):

$$-\hbar^2\frac{d^2}{dx^2}\left(e^{\frac{i}{\hbar}S(x)}\right) \;=\; p^2(x)e^{\frac{i}{\hbar}S(x)}\,. \tag{3.2.2}$$

Let us examine the left-hand side and take the two derivatives

$$-\hbar^2\frac{d^2}{dx^2}\left(e^{\frac{i}{\hbar}S(x)}\right) = -\hbar^2\frac{d}{dx}\left(\frac{i}{\hbar}S'(x)e^{\frac{i}{\hbar}S(x)}\right) = -\hbar^2\left(\frac{iS''}{\hbar} - \frac{(S')^2}{\hbar^2}\right)e^{\frac{i}{\hbar}S(x)}\,. \tag{3.2.3}$$

Back into the differential equation and canceling the common exponential

$$-\hbar^2\left(\frac{iS''}{\hbar} - \frac{(S')^2}{\hbar^2}\right) = p^2(x)\,. \tag{3.2.4}$$

With minor rearrangements we get our final form:

$$\boxed{(S'(x))^2 - i\hbar S''(x) = p^2(x)\,.} \tag{3.2.5}$$

The presence of an explicit $i$in the equation tells us that the solution for S, as expected, cannot be real. At first sight one may be baffled: we started with the linear Schrödinger equation for ψ and obtained a *nonlinear* equation for S! This is actually unavoidable when the variable ψ is parameterized as an exponential and reminds us that sometimes a change of variables can turn a linear equation into a nonlinear one and viceversa. The nonlinear equation (3.2.5) allows us set up an approximation scheme in which $\hbar$ is considered small and thus the term involving $S''(x)$ is small. We will argue that this is in fact true for slowly varying potentials.

Claim: $i\hbar S''$ small if $V(x)$ is slowly varying.

Indeed, if $V(x) = V_0$ is a constant, then the local momentum $p(x)$ is equal to a constant p_0. Equation (3.2.5) is then solved by taking $S' = p_0$. For this choice $S'' = 0$ and the term $i\hbar S''$ vanishes identically for constant V. It should therefore be small for slowly varying $V(x)$.

Alternatively the term $i\hbar S''$ in the differential equation is small as $\hbar \to 0$, which makes the local de Broglie wavelength go to zero. In that case, the potential looks constant to the quantum particle.

We will thus take $\hbar$ to be the small parameter in a systematic expansion of $S(x)$:

$$S(x) \;=\; S_0(x) + \;\hbar S_1(x) + \;\hbar^2 S_2(x) + \mathcal{O}(\hbar^3)\,. \tag{3.2.6}$$

Here S_0, just like S, has units of $\hbar$. The next correction S_1 has no units, and the following, S_2 has units of one over $\hbar$. Now plug this expansion into our nonlinear equation (3.2.5)

$$\left(S_0' + \hbar S_1' + \hbar^2 S_2' + \ldots\right)^2 - i\hbar\left(S_0'' + \hbar S_1'' + \hbar^2 S_2'' + \ldots\right) \;-\; p^2(x) \;=\; 0\,. \tag{3.2.7}$$

The left-hand side is a power series expansion in $\hbar$. Just as we argued for the parameter λ in perturbation theory, here we want the left-hand side to vanish for all values of $\hbar$ and this requires that the coefficient of each power of $\hbar$ vanishes. We thus sort the left-hand side terms neglecting terms of order $\hbar^2$ or higher. We find

$$(S_0')^2 - p^2 \;+\; \hbar\left(2S_0'S_1' - iS_0''\right) + \mathcal{O}\left(\hbar^2\right) = 0 \tag{3.2.8}$$

This gives two equations, one for the coefficient of $(\hbar)^0$ and another for the coefficient of $\hbar$:

$$\begin{aligned} (S_0')^2 - p^2(x) \;&= 0\,, \\ 2S_0'S_1' - iS_0'' \;&= 0\,. \end{aligned} \tag{3.2.9}$$

The first equation is easily solved:

$$S_0' = \pm p(x) \quad \rightarrow \quad S_0(x) = \pm\int_{x_0}^{x} p(x')dx' \tag{3.2.10}$$

where x_0 is a constant of integration to be adjusted. The next equation allows us to find S_1 which is in fact imaginary:

$$S_1' = \frac{i}{2}\frac{S_0''}{S_0'} = \frac{i}{2}\frac{(\pm p'(x))}{(\pm p(x))} = \frac{i}{2}\frac{p'}{p}\,. \tag{3.2.11}$$

This is readily solved to give

$$i\,S_1(x) \;=\; -\tfrac{1}{2}\ln\,p(x) + C'\,. \tag{3.2.12}$$

Let us now reconstruct the wavefunction to this order of approximation:

$$\psi(x) \;=\; \exp\left[\frac{i}{\hbar}(S_0 + \hbar S_1 + \mathcal{O}(\hbar^2))\right] \simeq \exp\left[\frac{i}{\hbar}S_0\right]\exp\left[iS_1\right] \tag{3.2.13}$$

Using our results for S_0 and S_1 we have that the approximate solution is

$$\psi(x) \;=\; \exp\left[\pm\frac{i}{\hbar}\int_{x_0}^{x} p(x')dx'\right]\exp\left[-\tfrac{1}{2}\log p(x) + C'\right]\,. \tag{3.2.14}$$

We thus have

$$\boxed{\psi(x) \;=\; \frac{A}{\sqrt{p(x)}}\exp\left[\pm\frac{i}{\hbar}\int_{x_0}^{x}p(x')dx'\right].} \tag{3.2.15}$$

This is the basic solution in the WKB approximation. We do not attempt to normalize this wavefunction because, in fact, the region of validity of this approximation is still unclear.

Observables for the basic solution:

i) Probability density:

$$\rho=\psi^*\psi=\frac{|A|^2}{p(x)} \;=\; \frac{|A|^2}{mv(x)}\,, \tag{3.2.16}$$

where $v(x)$ is the local classical velocity. Note that ρ is higher where v is small as the particle lingers in those regions and is more likely to be found there. This is an intuition we developed long ago and is justified by this result.

ii) Probability current: In the language of the polar decomposition (3.1.9) of the wavefunction the basic solution corresponds to

$$\mathcal{S}(x)=\int_{x_0}^{x}p(x')dx' \tag{3.2.17}$$

Note that, as anticipated below equation (3.1.15) the gradient of $\mathcal{S}$ in the basic solution is the local momentum. Recalling the result (3.1.14) for the current,

$$J \;=\; \rho\,\frac{1}{m}\frac{\partial\mathcal{S}}{\partial x}\,, \tag{3.2.18}$$

and therefore,

$$J(x) \;=\; \frac{|A|^2}{p(x)}\frac{p(x)}{m} \;=\; \frac{|A|^2}{m}\,. \tag{3.2.19}$$

The fact that the current is a constant should not have taken us by surprise. A position-dependent current for an energy eigenstate is not possible, as it would violate the current conservation equation $\partial_x J(x)+\partial_t\rho=0$, given that ρ is time independent.

We con now write the general solutions that can be built from the basic solution and apply to classically allowed and classically forbidden regions.

On the allowed region $E-V(x)>0$ we write $p^2(x)=\hbar^2k^2(x)$, with $k(x)>0$ and hence the general solution is a superposition of two basic solutions with waves propagating in opposite directions:

$$\psi(x)=\frac{A}{\sqrt{k(x)}}\exp\left[i\int_{x_0}^{x}k(x')dx'\right]+\frac{B}{\sqrt{k(x)}}\exp\left[-i\int_{x_0}^{x}k(x')dx'\right]. \tag{3.2.20}$$

Note that the first wave, with coefficient A moves to the right while the second wave, with coefficient B moves to the left. This can be seen by recalling that the above energy eigenstate $\psi(x)$ is accompanied by the time factor $e^{-iEt/\hbar}$ when forming a full solution of the Schrödinger equation. Moreover, the first phase (accompanying A) grows as x grows, while the second phase becomes more negative as x grows.

On the forbidden region $p^2 = -\hbar^2\kappa^2(x)$ so we can take $p(x) = i\kappa(x)$ in the solution, with $\kappa > 0$, to find

$$\psi(x) \;=\; \frac{C}{\sqrt{\kappa(x)}} \exp\left[\int_{x_0}^{x} \kappa(x')dx'\right] + \frac{D}{\sqrt{\kappa(x)}} \exp\left[-\int_{x_0}^{x} \kappa(x')dx'\right] \tag{3.2.21}$$

The argument of the first exponential becomes more positive as x grows. Thus the first term, with coefficient C, is an increasing function as x grows. The argument of the second exponential becomes more negative x grows. Thus the second term, with coefficient D, is a decreasing function as x grows.

3.2.1 Validity of the approximation

To understand more concretely the validity of our approximations, we reconsider the expansion (3.2.8) of the differential equation:

$$(S_0')^2 - p^2 \;+\; \hbar\left(2S_0'S_1' - iS_0''\right) + \mathcal{O}\left(\hbar^2\right) = 0 \tag{3.2.22}$$

We must have that the $\mathcal{O}(\hbar)$ terms in the differential equation are much smaller, in magnitude, than the $\mathcal{O}(1)$ terms. At each of these orders we have two terms that are set equal to each other by the differential equations. It therefore suffices to check that one of the $\mathcal{O}(\hbar)$ terms is much smaller than one of the $\mathcal{O}(1)$ terms. Thus, for example, we must have

$$|\hbar S_0'S_1'| \;\ll\; |S_0'|^2\,. \tag{3.2.23}$$

Canceling one factor of $|S_0'|$ and recalling that $|S_0'| = |p|$ we have

$$|\hbar S_1'| \;\ll\; |p|\,. \tag{3.2.24}$$

From (3.2.11) we note that $|S_1'| \sim |p'/p|$ and therefore we get

$$\left|\hbar\frac{p'}{p}\right| \;\ll\; |p|\,. \tag{3.2.25}$$

There are two useful ways to think about this relation. First we write it as

$$\left|\frac{\hbar}{p}\right|\left|\frac{dp}{dx}\right| \;\ll\; |p| \quad\rightarrow\quad \lambda\left|\frac{dp}{dx}\right| \ll |p| \tag{3.2.26}$$

which tells us that the changes in the local momentum over a distance equal to the de Broglie wavelength are small compared to the momentum. Alternatively we write (3.2.25) as follows:

$$\left|\hbar\frac{p'}{p^2}\right| \;\ll\; 1 \quad\rightarrow\quad \left|\hbar\frac{d}{dx}\frac{1}{p}\right| \;\ll\; 1\,. \tag{3.2.27}$$

This now means

$$\boxed{\left|\frac{d\lambda}{dx}\right| \ll 1\,.} \tag{3.2.28}$$

The de Broglie wavelength must vary slowly. Note the consistency with units, the left-hand side of the inequality being unit free. More intuitive, perhaps, is the version obtained by multiplying the above by λ

$$\left|\lambda\frac{d\lambda}{dx}\right| \ll \lambda\,. \tag{3.2.29}$$

This tells us that the variation of the de Broglie wavelength λ over a distance λ must be much smaller that λ.

It is not hard to figure out what the above constraints tell us about the rate of change of the potential. Finally connect to the potential. Taking one spatial derivative of the equation $p^2 = 2m(E - V(x))$ we get

$$|pp'| \;=\; m\left|\frac{dV}{dx}\right| \quad\rightarrow\quad \left|\frac{dV}{dx}\right| = \frac{1}{m}|pp'|\,. \tag{3.2.30}$$

Multiplying by the absolute value of $\lambda = h/p$

$$\lambda(x)\left|\frac{dV}{dx}\right| = \frac{2\pi\hbar}{m}|p'| \ll \frac{p^2}{m}\,, \tag{3.2.31}$$

where the last inequality follows from (3.2.25). Hence, we find that

$$\boxed{\lambda(x)\left|\frac{dV}{dx}\right| \;\ll\; \frac{p^2}{2m}\,.} \tag{3.2.32}$$

The change in the potential over a distance equal to the de Broglie wavelength must be much smaller than the kinetic energy. This is the precise meaning of a slowly changing potential in the WKB approximation.

The slow variation conditions needed for the basic WKB solutions to be accurate fail near turning points. This could be anticipated since at turning points the local momentum becomes zero and the de Broglie wavelength becomes infinite. Under general conditions, sufficiently near a turning point the potential $V(x)$ is approximately linear, as shown in Figure 3.1. We then have

$$V(x) - E \;=\; g(x-a)\,, \quad g > 0\,. \tag{3.2.33}$$

In the allowed region $x < a$ the local momentum is

$$p^2 \;=\; 2m((E - V(x)) \;=\; 2mg(a-x)\,. \tag{3.2.34}$$

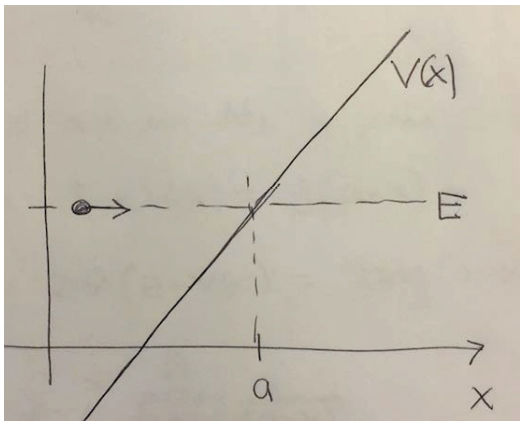


Figure 3.1: The slow-varying conditions in WKB are violated at turning points.

As a result, the de Broglie wavelength is given by

$$\lambda(x) \;=\; \frac{2\pi\hbar}{p} \;=\; \frac{2\pi\hbar}{\sqrt{2mg}\sqrt{a-x}}\,. \tag{3.2.35}$$

Taking a derivative, we find

$$\Big|\frac{d\lambda}{dx}\Big| \;=\; \frac{\pi\hbar}{\sqrt{2mg}}\frac{1}{(a-x)^{3/2}}\,. \tag{3.2.36}$$

The right-hand side goes to infinity as $x \to a$ and therefore the key condition (3.2.28) is violated as we approach turning points. Our basic WKB solutions can be valid only as long as we remain away from turning points. If we have a turning point, such as $x = a$ in the figure, we need a 'connection formula' that tells us how a solution far to the left and a solution far to the right of the turning point are related when they together form a single solution. We will consider a connection formula right below.

3.3 Connection formula

Let us first explain and then use a set of connection formulae, leaving their derivation for next section. The connection formulae refer to solutions away from a turning point $x = a$ separating a classically allowed region to the left and a classically forbidden region to the right. This is the situation illustrated in Figure 3.2.

For such turning point at $x = a$ the WKB solutions to the right are exponentials that grow or decay and the WKB solutions to the left are oscillatory functions. They connect

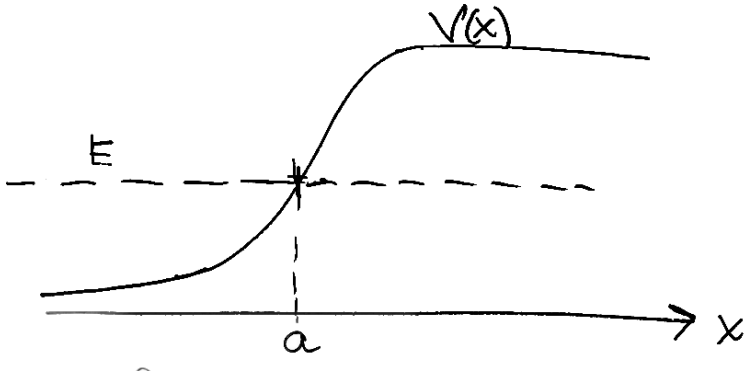


Figure 3.2:

consistent with the following relations

$$\frac{2}{\sqrt{k(x)}}\cos\left(\int_x^a k(x')dx' - \frac{\pi}{4}\right) \Longleftarrow \frac{1}{\sqrt{\kappa(x)}}\exp\left(-\int_a^x \kappa(x')dx'\right) \tag{3.3.1}$$

$$-\frac{1}{\sqrt{k(x)}}\sin\left(\int_x^a k(x')dx' - \frac{\pi}{4}\right) \Longrightarrow \frac{1}{\sqrt{\kappa(x)}}\exp\left(\int_a^x \kappa(x')dx'\right) \tag{3.3.2}$$

In the first relation the arrow tells us that if the solution is a pure decaying exponential to the right of $x = a$ the solution to the left of $x = a$ is accurately determined and given by the phase-shifted cosine function the arrow points to. The second relation says that if the solution to the left of $x = a$ is of an oscillatory type, the *growing part* of the solution to the right of $x = a$ is accurately determined and given by the exponential the arrow points to. The decaying part cannot be reliably determined. As we will elaborate upon later, any connection formula is not to be used in the direction that goes against the arrow.

Example: Find a quantization condition for the energies of bound states in a monotonically increasing potential $V(x)$ that has a hard wall at $x = 0$. Assume $V(x)$ increases without bound, as illustrated in Figure 3.3.

Let E denote the energy of our searched-for eigenstate. Clearly, the energy and the potential $V(x)$ determine the turning point $x = a$. The solution for $x > a$ must only have a decaying exponential since the forbidden region extends forever to the right of $x = a$. The wavefunction for $x > a$ is therefore of the type on the right-side of the connection formula (3.3.1). This means that we have an accurate representation of the wavefunction to the left of $x = a$. Adjusting the arbitrary normalization, we have

$$\psi(x) = \frac{1}{\sqrt{k(x)}}\cos\left(\int_x^a k(x')dx' - \tfrac{\pi}{4}\right), \quad 0 \le x \ll a\,. \tag{3.3.3}$$

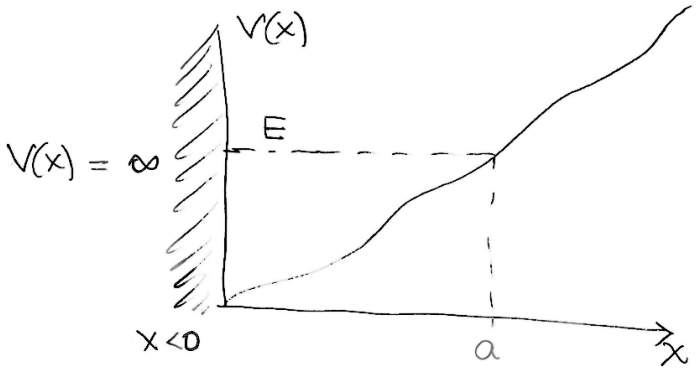


Figure 3.3: A monotonically increasing potential with a hard wall at $x = 0$. For an energy eigenstate of energy E the turning point is at $x = a$.

Since we have a hard wall, the wavefunction must vanish for $x = 0$. The condition $\psi(0) = 0$ requires that

$$\cos\Delta = 0\,, \quad \text{with} \quad \Delta = \int_0^a k(x')dx' - \tfrac{\pi}{4}\,. \tag{3.3.4}$$

This is satisfied when

$$\Delta = \int_0^a k(x')dx' - \tfrac{\pi}{4} \;=\; \tfrac{\pi}{2} + n\pi\,, \quad n \in \mathbb{Z}\,. \tag{3.3.5}$$

The quantization condition is therefore

$$\boxed{\int_0^a k(x')dx' = \left(n + \tfrac{3}{4}\right)\pi\,, \quad n = 0, 1, 2, \ldots\,.} \tag{3.3.6}$$

Negative integers are not allowed because the left-hand side is manifestly positive. The above is easy to use in practice. Using the expression for $k(x)$ in terms of E and $V(x)$ we have

$$\int_0^a \sqrt{\frac{2m}{\hbar^2}(E - V(x'))}\,dx' = \left(n + \tfrac{3}{4}\right)\pi\,, \quad n = 0, 1, 2, \ldots \tag{3.3.7}$$

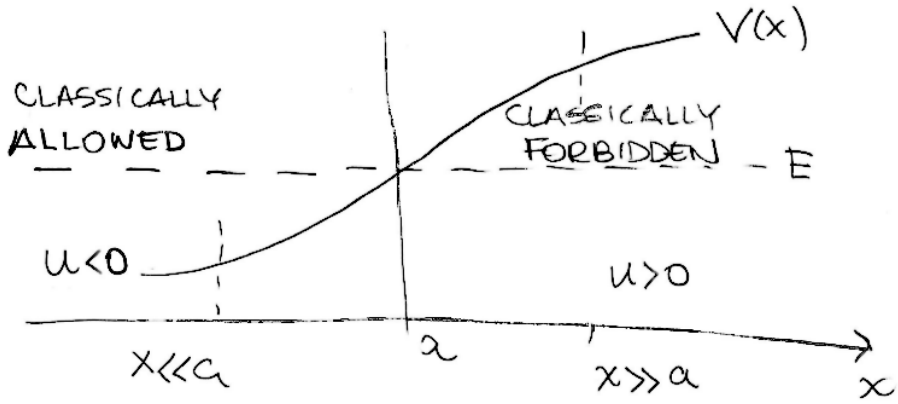
In some special cases a can be calculated in terms of E and the integral can be done analytically. More generally, this is done numerically, exploring the value of the integral on the left hand side as a function of E and selecting the energies for which it takes the quantized values on the right-hand side.

Let us rewrite the wavefunction using $\int_x^a = \int_0^a - \int_0^x$:

$$\begin{aligned}\psi(x) &= \frac{1}{\sqrt{k(x)}}\cos\left(\int_0^a k(x')dx' - \tfrac{\pi}{4} - \int_0^x k(x')dx'\right)\\ &= \frac{1}{\sqrt{k(x)}}\cos\left(\Delta - \int_0^x k(x')dx'\right)\\ &= \frac{\sin\Delta}{\sqrt{k(x)}}\sin\left(\int_0^x k(x')dx'\right),\end{aligned} \tag{3.3.8}$$

where we expanded the cosine of a sum of angles and recalled that $\cos\Delta = 0$. In this form it is manifest that the wavefunction vanishes at $x = 0$. More interestingly, the quantization condition (3.3.6) indicates that the excursion of the phase in the solution from 0 to a is a bit higher than $n\pi$ (but less than $(n+1)\pi$). Thus the WKB wavefuntion produces the n nodes the n-th excited state must have, even though this wavefunction is not reliable all to way to $x = a$.

3.4 Airy functions and connection formulae



(3.4.9)

$$V(x) - E \simeq g(x-a) \qquad \text{with } g > 0 \text{ for } x \sim a \tag{3.4.10}$$

Solutions

$$\psi(x) = \frac{A}{\sqrt{\kappa(x)}}\exp\left(-\int_a^x \kappa(x')dx'\right) + \frac{B}{\sqrt{\kappa(x)}}\exp\left(\int_a^x \kappa(x')dx'\right) \qquad x \gg a \tag{3.4.11}$$

$$\psi(x) = \frac{C}{\sqrt{k(x)}}\exp\left(i\int_x^a k(x')dx'\right) + \frac{D}{\sqrt{k(x)}}\exp\left(-i\int_x^a k(x')dx'\right) \qquad x \ll a \tag{3.4.12}$$

where

$$k^2 \equiv \frac{2m}{\hbar^2}(E - V(x)) \simeq \frac{2mg}{\hbar^2}(a - x) \quad x \leq a \tag{3.4.13}$$

$$\kappa^2 \equiv \frac{2m}{\hbar^2}(V(x) - E) \simeq \frac{2mg}{\hbar^2}(x - a) \quad x \geq a \tag{3.4.14}$$

Idea: Solve Schrodinger equation

$$-\frac{\hbar^2}{2m}\psi'' + (V(x) - E)\psi = 0 \tag{3.4.15}$$

with the exact linear potential, i.e.

$$-\frac{\hbar^2}{2m}\psi'' + g(x - a)\psi = 0 \tag{3.4.16}$$

- Solve (3.4.16) exactly.
- Match it to the $x \gg a$ version of (3.4.11) or $x \ll a$ version of (3.4.12).
- Find the required relations between coefficients!

Solve (3.4.16). Remove units, find length scale.

$$\frac{\hbar^2}{mL^2} = gL \implies L = \left(\frac{\hbar^2}{mg}\right)^{\frac{1}{3}} \tag{3.4.17}$$

so define

$$u = \left(\frac{2mg}{\hbar^2}\right)^{\frac{1}{3}}(x - a) \equiv \eta(x - a) \tag{3.4.18}$$

thus (3.4.16) becomes

$$\boxed{\frac{d^2\psi}{du^2} - u\psi = 0} \tag{3.4.19}$$

with solution

$$\psi = \alpha A_i(u) + \beta B_i(u) \tag{3.4.20}$$

where α and β are constants and $A_i(u)$, $B_i(u)$ are Airy functions:

$$A_i(u) \simeq \begin{cases} \frac{1}{2}\frac{1}{\sqrt{\pi}}|u|^{-\frac{1}{4}}e^{-\xi} & u \gg 1, \\ \frac{1}{\sqrt{\pi}}|u|^{-\frac{1}{4}}\cos\left(\xi - \frac{\pi}{4}\right) & u \ll -1. \end{cases} \tag{3.4.21}$$

$$B_i(u) \simeq \begin{cases} \frac{1}{\sqrt{\pi}}|u|^{-\frac{1}{4}}e^{\xi} & u \gg 1, \\ -\frac{1}{\sqrt{\pi}}|u|^{-\frac{1}{4}}\sin\left(\xi - \frac{\pi}{4}\right) & u \ll -1. \end{cases} \tag{3.4.22}$$

with

$$\xi \equiv \frac{2}{3}|u|^{\frac{3}{2}}\,. \tag{3.4.23}$$

These are in fact WKB solutions and special cases of connection conditions! (Explain)

3.4.1 How bad are the errors?

Take a WKB solution and find the DE it satisfies

$$\psi(u) = \frac{1}{u^{\frac{1}{4}}} e^{-\frac{2}{3}|u|^{\frac{3}{2}}} \tag{3.4.24}$$

solves

$$\frac{d^2\psi}{du^2} - \Big(u + \frac{5}{16}\frac{1}{u^2}\Big)\psi = 0 \tag{3.4.25}$$

so clearly for $u \gg 1$ the extra term is negligible.

To evaluate (3.4.11) and (3.4.12), determine $\kappa(x)$ and $k(x)$. Using (3.4.13) and (3.4.14):

$$k^2 = \eta^3(a-x) = -\eta^2 u = \eta^2|u| \qquad u < 0 \tag{3.4.26}$$

$$\kappa^2 = \eta^3(x-a) = +\eta^2 u \qquad u > 0 \tag{3.4.27}$$

Using $' = \frac{d}{dx}$, the WKB condition is $|k'| \ll |k^2|$ From ...

$$|2kk'| = \eta^3 \implies |k'| = \frac{\eta^3}{2|k|} = \frac{\eta^3}{2\eta|u|} = \frac{\eta^2}{2|u|} \tag{3.4.28}$$

$k^2 = \eta^2|u|$ thus

$$|k'| \ll k^2\,, \frac{\eta^2}{2|u|} \ll \eta^2|u| \implies |u|^{\frac{3}{2}} \gg \frac{1}{2} \implies |u| \gg 0.63 \tag{3.4.29}$$

Two integrals to estimate

$$x > a: \qquad \int_a^x \kappa(x')dx' = \int_a^x \sqrt{\eta^3(x'-a)}dx' = \frac{2}{3}\eta^{\frac{3}{2}}(x'-a)^{\frac{3}{2}}\Big|_a^x$$
$$= \frac{2}{3}\eta^{\frac{3}{2}}(x-a)^{\frac{3}{2}} = \frac{2}{3}u^{\frac{3}{2}} = \frac{2}{3}|u|^{\frac{3}{2}} = \xi \tag{3.4.30}$$

$$x < a: \qquad \int_x^a k(x')dx' = \int_x^a \sqrt{\eta^3(a-x')}dx' = \eta^{\frac{3}{2}}\left[-\frac{2}{3}(a-x')^{\frac{3}{2}}\right]_x^a$$
$$= \frac{2}{3}\eta^{\frac{3}{2}}(a-x)^{\frac{3}{2}} = \frac{2}{3}|u|^{\frac{3}{2}} = \xi \tag{3.4.31}$$

both integrals are equal to ξ.

$$\frac{1}{\sqrt{\kappa(x)}} = \frac{1}{\eta^{\frac{1}{2}}|u|^{\frac{1}{4}}}\,, \qquad \frac{1}{\sqrt{k(x)}} = \frac{1}{\eta^{\frac{1}{2}}|u|^{\frac{1}{4}}} \tag{3.4.32}$$

(3.4.11) and (3.4.12), let $\{A,B,C,D\} \to \eta^{\frac{1}{2}}\{A,B,C,D\}\frac{1}{\sqrt{\pi}}$ to cancel the extra factor and produce the ... constants

$$\begin{aligned}\psi(x) &= A\frac{|u|^{-\frac{1}{4}}}{\sqrt{\pi}}e^{-\xi} + B\frac{|u|^{-\frac{1}{4}}}{\sqrt{\pi}}e^{\xi} \qquad u \gg 1 \\ &= 2AA_i(u) + BB_i(u) \end{aligned} \tag{3.4.33}$$

$$\psi(x) = C\frac{|u|^{-\frac{1}{4}}}{\sqrt{\pi}}e^{i\xi} + D\frac{|u|^{-\frac{1}{4}}}{\sqrt{\pi}}e^{-i\xi} \qquad u \ll -1 \tag{3.4.34}$$

Note that

$$A_i + iB_i = \frac{|u|^{-\frac{1}{4}}}{\sqrt{\pi}}e^{-i(\xi-\frac{\pi}{4})} \tag{3.4.35}$$

$$A_i - iB_i = \frac{|u|^{-\frac{1}{4}}}{\sqrt{\pi}}e^{i(\xi-\frac{\pi}{4})} \tag{3.4.36}$$

thus

$$e^{i\frac{\pi}{4}}(A_i - iB_i) = \frac{|u|^{-\frac{1}{4}}}{\sqrt{\pi}}e^{i\xi} \tag{3.4.37}$$

$$e^{-i\frac{\pi}{4}}(A_i + iB_i) = \frac{|u|^{-\frac{1}{4}}}{\sqrt{\pi}}e^{-i\xi} \tag{3.4.38}$$

Now back in (3.4.34):

$$\begin{aligned}\psi(x) &= Ce^{i\frac{\pi}{4}}(A_i - iB_i) + De^{-i\frac{\pi}{4}}(A_i + iB_i) \\ &= \left(Ce^{i\frac{\pi}{4}} + De^{-i\frac{\pi}{4}}\right)A_i + \left(iDe^{-i\frac{\pi}{4}} - iCe^{i\frac{\pi}{4}}\right)B_i \end{aligned} \tag{3.4.39}$$

Finally equate (one solution):

$$2A = Ce^{i\frac{\pi}{4}} + De^{-i\frac{\pi}{4}} \tag{3.4.40}$$

$$iB = Ce^{i\frac{\pi}{4}} - De^{-i\frac{\pi}{4}} \implies \tag{3.4.41}$$

$$C = \frac{1}{2}e^{-i\frac{\pi}{4}}(2A + iB) \tag{3.4.42}$$

$$D = \frac{1}{2}e^{i\frac{\pi}{4}}(2A - iB) \tag{3.4.43}$$

back in (3.4.12)

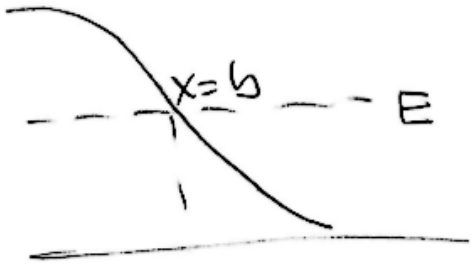
$$\psi(x) = \frac{1}{2}\frac{(2A+iB)}{\sqrt{k(x)}}\exp\left(i\int_x^a k(x')dx' - \frac{\pi}{4}\right) + \frac{1}{2}\frac{(2A-iB)}{\sqrt{k(x)}}\exp\left(-i\int_x^a k(x')dx' - \frac{\pi}{4}\right) \implies$$

$$\boxed{\psi(x) = \frac{2A}{\sqrt{k(x)}} \cos\left(\int_x^a k(x')dx' - \frac{\pi}{4}\right) - \frac{B}{\sqrt{k(x)}} \sin\left(\int_x^a k(x')dx' - \frac{\pi}{4}\right)} \tag{3.4.44}$$

Now discuss a subtlety. The formulas are in reality only usable in one direction with partial results. Some terminology helps. We always speak having in mind a fixed turning point. If we say we have a growing exponential at a turning point we mean we have a solution that grows as we move *away* from the turning point towards the classically forbidden region. Similarly, a decaying exponential means our solution decays as we move *away* from the turning point towards the classically forbidden region. In summary the connection arrow can go from a decaying exponential into an oscillatory solution and can go from an oscillatory solution into a growing exponential.

3.4.2 The other connection conditions

This time the turning point is at $x = b$, with the classically allowed region to the right of it and the classically forbidden region to the left of it.



$$\frac{1}{\sqrt{\kappa(x)}} \exp\left(-\int_x^b \kappa(x')dx'\right) \implies \frac{2}{\sqrt{k(x)}} \cos\left(\int_b^x k(x')dx' - \frac{\pi}{4}\right) \tag{3.4.45}$$

$$-\frac{1}{\sqrt{\kappa(x)}} \exp\left(\int_x^b \kappa(x')dx'\right) \impliedby \frac{1}{\sqrt{k(x)}} \sin\left(\int_b^x k(x')dx' - \frac{\pi}{4}\right) \tag{3.4.46}$$

For the first relation, if there is *only* a decaying exponential to the left, the wavefunction is definitely without the growing exponential, and the wavefunction to the right of $x = b$ is accurately determined. This does not work in the reverse direction because a small error in the oscillatory function would give a growing exponential to the left of for $x = b$ that would overtake the predicted decaying solution.

For the second relation, the stated direction (from right to left) is reliable: an small error on the right side of $x = b$ would produce a decaying exponential, thus a small error on the left-side of $x = b$. The reverse direction does not work: a small error to the left of $x = b$, a decaying exponential, would produce a large error in the right-hand side.

In summary, in *all cases* of the connection conditions, relative to a turning point,

We can connect away from a decaying exponential and into a growing exponential.

(3.4.47)

3.5 Tunnelling through a barrier

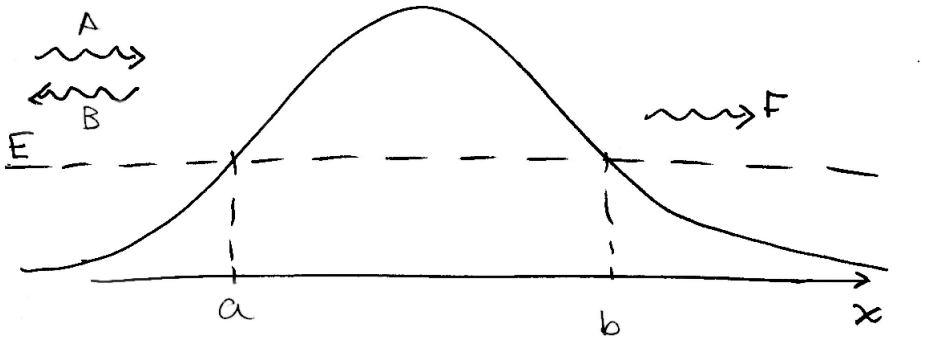


Figure 3.4: Tunneling in the WKB approximation. The energy E must be smaller than the height of the potential, and the barrier must be wide and smooth.

We want to find the tunneling probability T for a wave of energy incident on a smoothly varying wide barrier. The energy E of the wave must be smaller than the height of the potential. In this problem there is an incident wave, a reflected wave and a transmitted wave, and the associated WKB expressions will have amplitudes controlled by constants A, B, and F, respectively. The situation is illustrated in Figure 3.4.
Remarks:

1) Expect T to be small. Little probability flux goes through and $|A| \approx |B|$.

2) For $x \gg b$ there is just an outgoing wave with amplitude controlled by F.

3) Within the barrier the component that decays as x grows is more relevant that the component that grows. It is the only component that can be estimated reliably.

Consider the transmitted right-moving wave valid for $x \gg b$

$$\psi_{tr}(x) \;=\; \frac{F}{\sqrt{k(x)}} \exp\left(i \int_b^x k(x')dx' - i\tfrac{\pi}{4} \right) \;, \quad x \gg b\,. \tag{3.5.1}$$

This is a WKB solution with an extra phase of $\pi/4$ chosen to make the argument of the exponential have the familiar form appearing in the connection formulae. Expanding the

exponential

$$\psi_{tr}(x) = \frac{F}{\sqrt{k(x)}} \cos\left(\int_b^x k(x')dx' - \tfrac{\pi}{4}\right) + \frac{iF}{\sqrt{k(x)}} \sin\left(\int_b^x k(x')dx' - \tfrac{\pi}{4}\right) \ , \ \ x \gg b \, . \quad (3.5.2)$$

This is in *standard form*. We can now match the second term to an exponential that grows as we move to the left of $x = b$, by using (3.4.46)

$$\psi(x)_{barr} = -\frac{iF}{\sqrt{\kappa(x)}} \exp\left(\int_x^b \kappa(x')dx'\right) \ , \quad a \ll x \ll b \ . \quad (3.5.3)$$

The subscript 'barr' indicates a solution in the barrier region. If we attempted to match the first term in (3.5.2) we would get an exponential that decays as we move to the left of $x = b$ and it is unreliable given the growing exponential. We can now refer this solution to the point $x = a$

$$\psi(x)_{barr} = -\frac{iF}{\sqrt{\kappa(x)}} \exp\left(\int_a^b \kappa(x')dx' - \int_a^x \kappa(x')dx'\right) \quad a \ll x \ll b \, . \quad (3.5.4)$$

Defining

$$\theta \equiv \int_a^b \kappa(x')dx' \quad (3.5.5)$$

we have

$$\psi(x)_{barr} = -\frac{iFe^{\theta}}{\sqrt{\kappa(x)}} \exp\left(-\int_a^x \kappa(x')dx'\right) \quad a \ll x \ll b \, . \quad (3.5.6)$$

Since this is a decaying exponential to the right of $x > a$ we can connect it to a solution to the left of $x < a$ using (3.3.1)

$$\psi(x) = -\frac{2iFe^{\theta}}{\sqrt{k(x)}} \cos\left(\int_x^a k(x')dx' - \tfrac{\pi}{4}\right) \, . \quad (3.5.7)$$

This is a superposition of two waves, a wave ψ_{inc} incident on the barrier and a wave ψ_{ref} reflected from the barrier. The incident part is

$$\psi_{inc}(x) = -\frac{iFe^{\theta}}{\sqrt{k(x)}} \exp\left(-i\int_x^a k(x')dx' + i\tfrac{\pi}{4}\right) \, . \quad (3.5.8)$$

The sign in front of the integral may seem unusual for a wave moving to the right, but it is correct because the argument x appears in the lower limit of the integration. The transmission coefficient T is the ratio of the transmitted probability current over the incident probability current. Given the result in (3.2.19) we have

$$T \ = \ \frac{\text{probability current for } \psi_{tr}}{\text{probability current for } \psi_{inc}} \ = \ \frac{|F|^2}{|-iFe^{\theta}|^2} \ = \ e^{-2\theta} \, . \quad (3.5.9)$$

This is the well-known exponential suppression of the transmission coefficient. Using the earlier definition of θ the result is

$$T_{\rm wkb} \;=\; \exp\Big(-2\int_a^b \kappa(x')dx'\Big)\,. \tag{3.5.10}$$

We added the subscript 'wkb' to emphasize that this is the WKB approximation to the exact transmission coefficient. The integral extends in between the two turning points and captures information about the height and the width of the barrier. The integrand, as well as the turning points, depend on the energy as we can display by using the explicit value of $\kappa(x)$:

$$T_{\rm wkb} \;=\; \exp\Big(-2\int_a^b \sqrt{\frac{2m}{\hbar^2}(V(x')-E)}\;\,dx'\Big)\,. \tag{3.5.11}$$

The WKB approximation only captures the exponentially decaying part of the transmission coefficient. There are corrections that are written as a prefactor to the exponential. These are not determined in this approximation.

Example. Use the WKB approximation to estimate the transmission probability T for the rectangular barrier

$$V(x) \;=\; \begin{cases} V_0 & \text{for } \;|x|<a\,,\\ 0\,, & \text{otherwise.}\end{cases} \tag{3.5.12}$$

Assume the barrier is large. In terms of the familiar unit-free constant z_0 used to characterize square wells, this means that

$$z_0^2 \;\equiv\; \frac{2mV_0a^2}{\hbar^2} \gg 1\,. \tag{3.5.13}$$

Large barrier means large z_0 or large V_0a^2. Moreover we assume E smaller than V_0; we cannot expect the approximation to work as the energy approaches the top of the barrier. Compare the WKB result for T with the exact result.

Solution. The WKB estimation, using (3.5.11) is immediate. Since the barrier extends from $x=-a$ to $x=a$ and the potential is constant we have

$$T_{\rm wkb} \;=\; \exp\Big(-2\int_{-a}^{a} \sqrt{\frac{2m}{\hbar^2}(V_0-E)}\;\,dx'\Big)\,. \tag{3.5.14}$$

The integral can be done and we find

$$T_{\rm wkb} \;=\; \exp\Big(-\frac{4a}{\hbar}\sqrt{2m(V_0-E)}\;\Big)\,. \tag{3.5.15}$$

This is the answer in the WKB approximation. In terms of z_0 this reads

$$T_{\rm wkb} \;\simeq\; \exp\Big(-4z_0\sqrt{1-\frac{E}{V_0}}\;\Big)\,. \tag{3.5.16}$$

The validity of the WKB approximation requires the argument in the exponent to be large. This is why we need $z_0 \gg 1$ and the energy not to approach V_0. When E is very small compared to V_0, we have

$$T \sim \exp(-4z_0)\,. \tag{3.5.17}$$

Since $z_0 \sim a\sqrt{V_0}$, this result is the basis for the claim that the exponential suppression of the tunneling probability is proportional to the width of the well and the square root of its height.

The exact formula for the tunneling probability of a square barrier has been calculated before, and it is given by

$$\frac{1}{T} = 1 + \frac{V_0^2}{4E(V_0-E)} \sinh^2\Big(\frac{2a}{\hbar}\sqrt{2m(V_0-E)}\Big)\,. \tag{3.5.18}$$

This formula will allow us to confirm the WKB exponential suppression and to find the prefactor. Under the conditions $z_0 \gg 1$ and $V_0 - E$ finite, the argument of the sinh function is large so this function can be replaced by its growing exponential ($\sinh x \sim \frac{1}{2}e^x$):

$$\frac{1}{T} \simeq 1 + \frac{V_0}{16E(1-\frac{E}{V_0})} \exp\Big(\frac{4a}{\hbar}\sqrt{2m(V_0-E)}\Big)\,, \tag{3.5.19}$$

where we also replaced $V_0 - E \to V_0$ in the prefactor. The additive unit on the right-hand side can be neglected and we have

$$T \simeq 16\,\tfrac{E}{V_0}\,(1-\tfrac{E}{V_0})\,\exp\Big(-\frac{4a}{\hbar}\sqrt{2m(V_0-E)}\Big)\,. \tag{3.5.20}$$

This result gives the same in exponential suppression as the WKB result (3.5.15). It also gives us a good approximation to the prefactor.

The WKB approximation is often used for the estimation of lifetimes. The physical situation is represented in Figure 3.5. We have a particle of mass m and energy E localized between the turning points $x = a$ and $x = b$ of the potential. The classical particle cannot escape because of the energy barrier stretching from $x = b$ to $x = c$. The quantum particle, however, can tunnel. The state of the quantum particle when localized between a and b is not strictly an energy eigenstate because the wavefunction for any energy eigenstate is nonzero for $x > c$. Our goal is to determine the lifetime τ of the particle. This is done by using some classical estimates as well as the quantum transmission probability.

We first show that the lifetime τ is the inverse of $\mathcal{B}$, the tunneling probability per unit time. To see this we examine the function $P(t)$ that represents the probability to have the particle localized within $[a, b]$ at time t, if it was there at $t = 0$. The lifetime is said to be τ if $P(t)$ has the time dependence $P(t) = e^{-t/\tau}$. To see that we have such a situation when the tunneling rate $\mathcal{B}$ is constant note that

$$P(t+dt) = P(t) \cdot \big(\text{probability that it does not tunnel in the next } dt\,\big)\,. \tag{3.5.21}$$

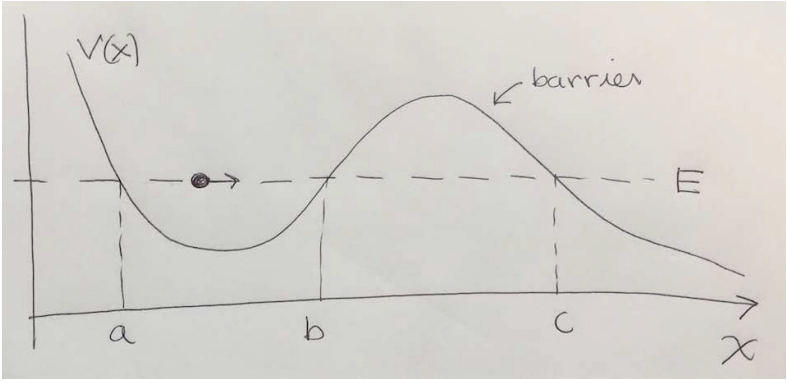


Figure 3.5: Estimating the lifetime of a particle with energy E temporarily localized in $x \in [a, b]$.

Therefore

$$P(t+dt) \;=\; P(t)\cdot\big(1-\mathcal{B}dt\big) \quad\to\quad P(t+dt)-P(t) \;=\; -\mathcal{B}P(t)\,dt\,. \tag{3.5.22}$$

We thus have the differential equation, and solution,

$$\frac{dP}{dt} \;=\; -\mathcal{B}\,P(t) \quad\to\quad P(t)=e^{-\mathcal{B}t}\,, \tag{3.5.23}$$

from which we identify, as claimed, that

$$\tau \;=\; \frac{1}{\mathcal{B}}\,. \tag{3.5.24}$$

The tunneling rate $\mathcal{B}$ or tunneling probability per unit time is estimated by counting the number of times $n_{\rm hit}$ the classical particle, bouncing between $x=a$ and $x=b$, hits the barrier at $x=b$ per unit time, and multiplying this number by the tunneling probability T:

$$\mathcal{B}=n_{\rm hit}\,T \;=\; \frac{T}{\Delta t}\,, \tag{3.5.25}$$

where Δt is the time the classical particle takes to go from b to a and back to b:

$$\Delta t \;=\; 2\int_a^b \frac{dx}{v(x)} \;=\; 2m\int_a^b \frac{dx}{p(x)}\,. \tag{3.5.26}$$

We now can put all the pieces together, using the WKB approximation for T. We find

$$\tau \;=\; \frac{\Delta t}{T} \simeq\; 2m\int_a^b \frac{dx}{p(x)}\cdot\exp\Big(2\int_b^c \kappa(x)dx\Big)\,. \tag{3.5.27}$$

The smaller the tunneling probability, the larger the lifetime of the localized state. Note that the factor Δt carries the units of the result. The above result can easily fail to be accurate, as the WKB approximation for T does not give the prefactor multiplying the exponential suppression.

Chapter 4

Time Dependent Perturbation Theory

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4.1 Time dependent perturbations

We will assume that, as before, we have a Hamiltonian $H^{(0)}$ that is known and is *time independent*. Known means we know the spectrum of energy eigenstates and the energy eigenvalues. This time the perturbation to the Hamiltonian, denoted as $\delta H(t)$ will be time dependent and, as a result, the full Hamiltonian $H(t)$ is also time dependent

$$H(t) = H^{(0)} + \delta H(t)\,. \tag{4.1.1}$$

While $H^{(0)}$ has a well-defined spectrum, $H(t)$ does not. Being time dependent, $H(t)$ does not have energy eigenstates. It is important to remember that the existence of energy eigenstates was predicated on the factorization of solutions $\Psi(x,t)$ of the full Schrödinger equation into a space-dependent part $\psi(x)$ and a time dependent part that turned out to be $e^{-iEt/\hbar}$, with E the energy. Such factorization is not possible when the Hamiltonian is time dependent. Since $H(t)$ does not have energy eigenstates the goal is to find the solutions $|\Psi(x,t)\rangle$ directly. Since we are going to focus on the time dependence, we will suppress the labels associated with space. We simply say we are trying to find the solution $|\Psi(t)\rangle$ to the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle \;=\; \big(H^{(0)} + \delta H(t)\big)|\Psi(t)\rangle\,. \tag{4.1.2}$$

In typical situations the perturbation $\delta H(t)$ vanishes for $t < t_0$, it exists for some finite time, and then vanishes for $t > t_f$ (see Figure 4.1). The system starts in an eigenstate of $H^{(0)}$ at $t < t_0$ or a linear combination thereof. We usually ask: What is the state of the system for $t > t_f$? Note that both initial and final states are nicely described in terms of eigenstates of $H^{(0)}$ since this *is* the Hamiltonian for $t < t_0$ and $t > t_f$. Even during the

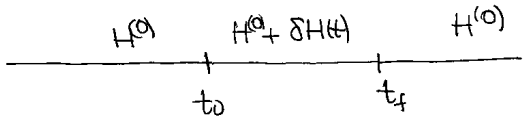


Figure 4.1: Time dependent perturbations typically exist for some time interval, here from t_0 to t_f.

time when the perturbation is on we can use the eigenstates of $H^{(0)}$ to describe the system, since these eigenstates form a complete basis, but the time dependence is very nontrivial.

Many physical questions can be couched in this language. For example, assume we have a hydrogen atom in its ground state. We turn on EM fields for some time interval. We can then ask: What are the probabilities to find the atom in each of the various excited states after the perturbation turned off?

4.1.1 The interaction picture

In order to solve efficiently for the state $|\Psi(t)\rangle$ we will introduce the *Interaction Picture* of Quantum Mechanics. This picture uses some elements of the Heisenberg picture and some elements of the Schrödinger picture. We will use the known Hamiltonian $H^{(0)}$ to define some Heisenberg operators and the perturbation δH will be used to write a Schrödinger equation.

We begin by recalling some facts from the Heisenberg picture. For *any* Hamiltonian, time dependent or not, one can determine the unitary operator $\mathcal{U}(t)$ that generates time evolution:

$$|\Psi(t)\rangle \;=\; \mathcal{U}(t)|\Psi(0)\rangle\,. \tag{4.1.3}$$

The Heisenberg operator $\hat{A}_H$ associated with a Schrödinger operator $\hat{A}_s$ is obtained by considering a rewriting of expectation values:

$$\langle\Psi(t)|\hat{A}_s|\Psi(t)\rangle = \langle\Psi(0)|\mathcal{U}^\dagger(t)\hat{A}_s\mathcal{U}(t)|\Psi(0)\rangle \;=\; \langle\Psi(0)|\hat{A}_H|\Psi(0)\rangle\,, \tag{4.1.4}$$

where

$$A_H \;\equiv\; \mathcal{U}^\dagger(t)\hat{A}_s\mathcal{U}(t)\,. \tag{4.1.5}$$

This definition applies even for time dependent Schrödinger operators. Note that the operator $\mathcal{U}^\dagger$ brings states to rest:

$$\mathcal{U}^\dagger(t)|\Psi(t)\rangle = \mathcal{U}^\dagger(t)\mathcal{U}(t)|\Psi(0)\rangle = |\Psi(0)\rangle\,. \tag{4.1.6}$$

In our problem the known Hamiltonian $H^{(0)}$ is time independent and the associated unitary time evolution operator $\mathcal{U}_0(t)$ takes the simple form

$$\mathcal{U}_0(t) = \exp\left(-\frac{iH^{(0)}t}{\hbar}\right). \tag{4.1.7}$$

The state $|\Psi(t)\rangle$ in our problem evolves through the effects of $H^{(0)}$ plus δH. Motivated by (4.1.6) we define the auxiliary ket $\big|\widetilde{\Psi}(t)\big\rangle$ as the ket $|\Psi(t)\rangle$ partially brought to rest through $H^{(0)}$:

$$\boxed{\big|\widetilde{\Psi}(t)\big\rangle \equiv \exp\Big(\frac{iH^{(0)}t}{\hbar}\Big)\big|\Psi(t)\big\rangle\,.} \tag{4.1.8}$$

Expect that Schrödinger equation for $\big|\widetilde{\Psi}(t)\big\rangle$ will be simpler, as the above must have taken care of the time dependence generated by $H^{(0)}$. Of cours, if we can determine $\big|\widetilde{\Psi}(t)\big\rangle$ we can easily get back the desired state $\big|\Psi(t)\big\rangle$ inverting the above relation to find

$$\boxed{\big|\Psi(t)\big\rangle = \exp\Big(-\frac{iH^{(0)}t}{\hbar}\Big)\big|\widetilde{\Psi}(t)\big\rangle\,.} \tag{4.1.9}$$

Our objective now is to find the Schrödinger equation for $\big|\widetilde{\Psi}(t)\big\rangle$. Taking the time derivative of (4.1.8) and using (4.1.2)

$$\begin{aligned} i\hbar\frac{d}{dt}\big|\widetilde{\Psi}(t)\big\rangle &= -H^{(0)}\big|\widetilde{\Psi}(t)\big\rangle + \exp\Big(\frac{iH^{(0)}t}{\hbar}\Big)(H^{(0)}+\delta H(t))\big|\Psi(t)\big\rangle \\ &= \left[-H^{(0)} + \exp\Big(\frac{iH^{(0)}t}{\hbar}\Big)(H^{(0)}+\delta H(t))\exp\Big(-\frac{iH^{(0)}t}{\hbar}\Big)\right]\big|\widetilde{\Psi}(t)\big\rangle \\ &= \exp\Big(\frac{iH^{(0)}t}{\hbar}\Big)\delta H(t)\exp\Big(-\frac{iH^{(0)}t}{\hbar}\Big)\big|\widetilde{\Psi}(t)\big\rangle\,, \end{aligned} \tag{4.1.10}$$

where the dependence on $H^{(0)}$ cancelled out. We have thus found the Schrödinger equation

$$\boxed{i\hbar\frac{d}{dt}\big|\widetilde{\Psi}(t)\big\rangle = \widetilde{\delta H}(t)\big|\widetilde{\Psi}(t)\big\rangle\,.} \tag{4.1.11}$$

where the operator $\widetilde{\delta H}(t)$ is defined as

$$\boxed{\widetilde{\delta H}(t) \equiv \exp\Big(\frac{iH^{(0)}t}{\hbar}\Big)\delta H(t)\,\exp\Big(-\frac{iH^{(0)}t}{\hbar}\Big)\,.} \tag{4.1.12}$$

Note that as expected the time evolution left in $\big|\widetilde{\Psi}(t)\big\rangle$ is generated by $\widetilde{\delta H}(t)$ via a Schrödinger equation. The operator $\widetilde{\delta H}(t)$ is nothing else but the Heisenberg version of δH generated using $H^{(0)}$! This is an *interaction picture*, a mixture of Heisenberg's and Schrödinger picture. While we have some Heisenberg$^{(0)}$ operators there is still a time dependent state $\big|\widetilde{\Psi}(t)\big\rangle$ and a Schrödinger equation for it.

How does it all look in an orthonormal basis? Let $|n\rangle$ be the complete orthonormal basis of states for $H^{(0)}$:

$$H^{(0)}|n\rangle = E_n|n\rangle\,. \tag{4.1.13}$$

This time there is no need for a (0) superscript, since neither the states nor their energies will be corrected (there are no energy eigenstates in the time-dependent theory). We then write an ansatz for our unknown ket:

$$\big|\widetilde{\Psi}(t)\big\rangle = \sum_n c_n(t)|n\rangle\,. \tag{4.1.14}$$

Here the functions $c_n(t)$ are unknown. This expansion is justified since the states $|n\rangle$ form a basis, and thus at all times they can be used to describe the state of the system. The original wavefunction is then:

$$\big|\Psi(t)\big\rangle = \exp\Big(-\frac{iH^{(0)}t}{\hbar}\Big)\big|\widetilde{\Psi}(t)\big\rangle = \sum_n c_n(t)\exp\left(-\frac{iE_nt}{\hbar}\right)|n\rangle\,. \tag{4.1.15}$$

Note that the time dependence due to $H^{(0)}$ is present here. If we had $\delta H = 0$ the state $\big|\widetilde{\Psi}(t)\big\rangle$ would be a constant, as demanded by the Schrödinger equation (4.1.11) and the $c_n(t)$ would be constants. The solution above would give the expected time evolution of the states under $H^{(0)}$.

To see what the Schrödinger equation tells us about the functions $c_n(t)$ we plug the ansatz (4.1.14) into (4.1.11):

$$i\hbar\frac{d}{dt}\sum_m c_m(t)|m\rangle \;=\; \widetilde{\delta H}(t)\sum_n c_n(t)|n\rangle \tag{4.1.16}$$

Using dots for time derivatives and introducing a resolution of the identity on the right-hand side we find

$$\begin{aligned}\sum_m i\hbar\dot{c}_m(t)|m\rangle &= \sum_m |m\rangle\langle m|\widetilde{\delta H}(t)\sum_n c_n(t)|n\rangle \\ &= \sum_m |m\rangle\sum_n\langle m|\widetilde{\delta H}(t)|n\rangle c_n(t) \\ &= \sum_{m,n}\widetilde{\delta H}_{mn}(t)c_n(t)|m\rangle\,.\end{aligned} \tag{4.1.17}$$

Here we have used the familiar matrix element notation

$$\widetilde{\delta H}_{mn}(t) \equiv\; \langle m|\widetilde{\delta H}(t)|n\rangle\,. \tag{4.1.18}$$

Equating the coefficients of the basis kets $|m\rangle$ in (4.1.17) we get the equations

$$i\hbar\,\dot{c}_m(t) \;=\; \sum_n \widetilde{\delta H}_{mn}(t)\,c_n(t)\,. \tag{4.1.19}$$

The Schrödinger equation has become an infinite set of coupled first-order differential equations. The matrix elements in the equation can be simplified a bit by passing to un-tilde variables:

$$\begin{aligned}\widetilde{\delta H}_{mn}(t) &= \langle m| \exp\Big(\frac{iH^{(0)}t}{\hbar}\Big)\delta H(t)\, \exp\Big(-\frac{iH^{(0)}t}{\hbar}\Big)|n\rangle \\ &= \exp\left[\frac{i}{\hbar}(E_m - E_n)t\right]\langle m|\delta H(t)|n\rangle\,.\end{aligned} \tag{4.1.20}$$

If we define

$$\omega_{mn} \equiv \frac{E_m - E_n}{\hbar}\,, \tag{4.1.21}$$

we then have

$$\widetilde{\delta H}_{mn}(t) \;=\; e^{i\omega_{mn}t}\delta H_{mn}(t)\,. \tag{4.1.22}$$

The coupled equations (4.1.19) for the functions $c_n(t)$ then become

$$\boxed{\;i\hbar\,\dot{c}_m(t) \;=\; \sum_n e^{i\omega_{mn}t}\delta H_{mn}(t)c_n(t)\;.\;} \tag{4.1.23}$$

4.1.2 Example (based on Griffiths Problem 9.3)

Consider a two-state system with basis states $|a\rangle$ and $|b\rangle$, eigenstates of $H^{(0)}$ with energies E_a and E_b, respectively. Call

$$\omega_{ab} \equiv (E_a - E_b)/\hbar\,. \tag{4.1.24}$$

Now take the perturbation to be a matrix times a delta function at time equal zero. Thus the perturbation only exists for time equal zero:

$$\delta H(t) = \begin{pmatrix} 0 & \alpha \\ \alpha* & 0 \end{pmatrix}\delta(t) \equiv U\,\delta(t)\,, \tag{4.1.25}$$

where α is a complex number. With the basis vectors ordered as $|1\rangle = |a\rangle$ and $|2\rangle = |b\rangle$ we have

$$U \;=\; \begin{pmatrix} U_{aa} & U_{ab} \\ U_{ba} & U_{bb} \end{pmatrix}\,, \quad \text{with} \quad U_{aa} = U_{bb} = 0 \text{ and } U_{ab} = U_{ba}^* = \alpha\,. \tag{4.1.26}$$

There is a sudden violent perturbation at $t = 0$ with off-diagonal elements that should produce transition. Take the system to be in $|a\rangle$ for $t = -\infty$, what is the probability that it is in $|b\rangle$ for $t = +\infty$?

Solution: First note that if the system is in $|a\rangle$ at $t = -\infty$ it will remain in state $|a\rangle$ until $t = 0^-$, that is, just before the perturbation turns on. This is because $|a\rangle$ is an energy eigenstate of $H^{(0)}$. In fact we have, up to a constant phase,

$$|\Psi(t)\rangle \;=\; e^{-iE_at/\hbar}|a\rangle\,, \quad \text{for} \quad -\infty < t \le 0^-\,. \tag{4.1.27}$$

We are asked what will be the probability to find the state in $|b\rangle$ at $t = \infty$, but in fact, the answer is the same as the probability to find the state in $|b\rangle$ at $t = 0^+$. This is because the perturbation does not exist anymore and if the state at $t = 0^+$ is

$$|\Psi(0^+)\rangle \;=\; \gamma_a|a\rangle + \gamma_b\,|b\rangle\,, \tag{4.1.28}$$

with γ_1 and γ_2 constants, then the state for any time $t > 0$ will be

$$|\Psi(t)\rangle \;=\; \gamma_a|a\rangle e^{-iE_at/\hbar} + \gamma_b|b\rangle e^{-iE_bt/\hbar}\,. \tag{4.1.29}$$

The probability $p_b(t)$ to find the state $|b\rangle$ at time t will be

$$p_b(t) \;=\; |\langle b|\Psi(t)\rangle|^2 \;=\; \left|\gamma_b e^{-iE_bt/\hbar}\right| \;=\; |\gamma_b|^2\,, \tag{4.1.30}$$

and, as expected, this is time independent. It follows that to solve this problem we must just find the state at $t = 0^+$ and determine the constants γ_1 and γ_2.

Since we have two basis states the unknown tilde state is

$$\left|\widetilde{\Psi}(t)\right\rangle = c_a(t)|a\rangle + c_b(t)|b\rangle\,, \tag{4.1.31}$$

and the initial conditions are stating that the system begins in the state $|a\rangle$ are

$$c_a(0^-) = 1\,, \quad c_b(0^-) = 0\,. \tag{4.1.32}$$

The differential equations (4.1.23) take the form

$$\begin{aligned} i\hbar\,\dot{c}_a(t) \;&=\; e^{i\omega_{ab}t}\delta H_{ab}(t)c_b(t)\,,\\ i\hbar\,\dot{c}_b(t) \;&=\; e^{i\omega_{ba}t}\delta H_{ba}(t)c_a(t)\,. \end{aligned} \tag{4.1.33}$$

The couplings are off-diagonal because $\delta H_{aa} = \delta H_{bb} = 0$. Using the form of the δH matrix elements,

$$\begin{aligned} i\hbar\,\dot{c}_a(t) \;&=\; e^{i\omega_{ab}t}\;\;\alpha\,\delta(t)\;c_b(t)\,,\\ i\hbar\,\dot{c}_b(t) \;&=\; e^{-i\omega_{ab}t}\,\alpha^*\delta(t)\,c_a(t)\,. \end{aligned} \tag{4.1.34}$$

We know that for functions f continuous at $t = 0$ we have $f(t)\delta(t) = f(0)\delta(t)$. We now ask if we are allowed to use such identity for the right-hand side of the above equations. In fact we can use the identity for $e^{\pm i\omega_{ab}t}$ but not for the functions $c_a(t)$ and $c_b(t)$ that, are expected to be discontinuous at $t = 0$. They must be so, because they can only change at $t = 0$, when the delta function exists. Evaluating the exponentials at $t = 0$ we then get the simpler equations

$$\begin{aligned} i\hbar\,\dot{c}_a(t) \;&=\; \alpha\,\delta(t)\;c_b(t)\,,\\ i\hbar\,\dot{c}_b(t) \;&=\; \alpha^*\delta(t)\,c_a(t)\,. \end{aligned} \tag{4.1.35}$$

With such singular right-hand sides, the solution of these equations needs regulation. We will regulate the delta function and solve the problem. A consistency check is that the solution has a well-defined limit as the regulator is removed. We will replace the $\delta(t)$ by the function $\Delta_{t_0}(t)$, with $t_0 > 0$, defined as follows:

$$\delta(t) \;\to\; \Delta_{t_0}(t) \;=\; \begin{cases} 1/t_0\,, & \text{for } t\in[0,t_0]\,,\\ 0\,, & \text{otherwise}\,. \end{cases} \tag{4.1.36}$$

Note that as appropriate, $\int dt\Delta_{t_0}(t) = 1$, and that $\Delta_{t_0}(t)$ in the limit as $t_0 \to 0$ approaches a delta function. If we replace the delta functions in (4.1.37) by the regulator we find, for $t \in [0, t_0]$

$$\begin{aligned} \text{For } t\in[0,t_0]: \qquad i\hbar\,\dot{c}_a(t) &= \frac{\alpha}{t_0}\,c_b(t)\,,\\ i\hbar\,\dot{c}_b(t) &= \frac{\alpha^*}{t_0}\,c_a(t)\,. \end{aligned} \tag{4.1.37}$$

For any other times the right-hand side vanishes. By taking a time derivative of the first equation and using the second one we find that

$$\ddot{c}_a(t) \;=\; \frac{1}{i\hbar}\frac{\alpha}{t_0}\frac{1}{i\hbar}\frac{\alpha^*}{t_0}\,c_a(t) \;=\; -\left(\frac{|\alpha|}{\hbar t_0}\right)^2 c_a(t)\,. \tag{4.1.38}$$

This is a simple second order differential equation and its general solution is

$$c_a(t) = \beta_0\cos\left(\frac{|\alpha|t}{\hbar t_0}\right) + \beta_1\sin\left(\frac{|\alpha|t}{\hbar t_0}\right)\,. \tag{4.1.39}$$

This is accompanied with $c_b(t)$ which is readily obtained from the first line in (4.1.37):

$$c_b(t) \;=\; \frac{i\hbar t_0}{\alpha}\dot{c}_a(t) \;=\; \frac{i|\alpha|}{\alpha}\Big(-\beta_0\sin\Big(\frac{|\alpha|t}{\hbar t_0}\Big) + \beta_1\cos\Big(\frac{|\alpha|t}{\hbar t_0}\Big)\Big)\,. \tag{4.1.40}$$

The initial conditions (4.1.32) tell us that in this regulated problem $c_a(0) = 1$ and $c_b(0) = 0$. Given the solutions above, the first condition fixes $\beta_0 = 1$ and the second fixes $\beta_1 = 0$. Thus, our solutions are:

$$\text{For } t\in[0,t_0]: \qquad c_a(t) = \cos\left(\frac{|\alpha|t}{\hbar t_0}\right)\,, \tag{4.1.41}$$

$$c_b(t) = -i\frac{|\alpha|}{\alpha}\sin\left(\frac{|\alpha|t}{\hbar t_0}\right)\,. \tag{4.1.42}$$

When the (regulated) perturbation is turned off ($t = t_0$), c_a and c_b stop varying and the constant value they take is their values at $t = t_0$. Hence

$$c_a(t > t_0) = c_a(t_0) = \cos\left(\frac{|\alpha|}{\hbar}\right)\,, \tag{4.1.43}$$

$$c_b(t > t_0) = c_b(t_0) = -i\frac{|\alpha|}{\alpha}\sin\left(\frac{|\alpha|}{\hbar}\right)\,. \tag{4.1.44}$$

Note that these values are t_0 independent. Being regulator independent, we can safely take the limit $t_0 \to 0$ to get

$$c_a(t>0) = \cos\left(\frac{|\alpha|}{\hbar}\right) , \tag{4.1.45}$$

$$c_b(t>0) = -i\frac{|\alpha|}{\alpha}\sin\left(\frac{|\alpha|}{\hbar}\right) . \tag{4.1.46}$$

Our calculation above shows that at $t = 0^+$ the state will be

$$|\Psi(0^+)\rangle = |\widetilde{\Psi}(0^+)\rangle = \cos\left(\frac{|\alpha|}{\hbar}\right)\big|\, a\,\big\rangle \;-\; i\frac{|\alpha|}{\alpha}\sin\left(\frac{|\alpha|}{\hbar}\right)\big|\, b\,\big\rangle . \tag{4.1.47}$$

With only free evolution ensuing for $t > 0$ we have (as anticipated in (4.1.29))

$$|\Psi(t)\rangle = \cos\left(\frac{|\alpha|}{\hbar}\right)\big|\, a\,\big\rangle e^{-iE_a t/\hbar} \;-\; i\frac{|\alpha|}{\alpha}\sin\left(\frac{|\alpha|}{\hbar}\right)\big|b\big\rangle\, e^{-iE_b t/\hbar} . \tag{4.1.48}$$

The probabilities to be found in $|a\rangle$ or in $|b\rangle$ are time-independent, we are in a superposition of energy eigenstates! We can now easily calculate the probability $p_b(t)$ to find the system in $|b\rangle$ for $t > 0$ as well as the probability $p_a(t)$ to find the system in $|a\rangle$ for $t > 0$:

$$\begin{aligned} p_b(t) &= |\langle b|\Psi(t)\rangle|^2 = \sin^2\left(\frac{|\alpha|}{\hbar}\right) , \\ p_a(t) &= |\langle a|\Psi(t)\rangle|^2 = \cos^2\left(\frac{|\alpha|}{\hbar}\right) . \end{aligned} \tag{4.1.49}$$

Note that $p_a(t)+p_b(t) = 1$, as required. The above is the exact solution of this system. If we had worked in perturbation theory, we would be taking the strength $|\alpha|$ of the interaction to be small. The answers we would obtain would form the power series expansion of the above formulas in the limit as $|\alpha|/\hbar$ is small.

4.2 Perturbative solution

In order to set up the perturbative expansion properly we include a unit-free small parameter λ multiplying the perturbation δH in the time-dependent Hamiltonian (4.1.1):

$$H(t) = H^{(0)} + \lambda\delta H(t) . \tag{4.2.1}$$

With such a replacement the interaction picture Schrödinger equation for $|\widetilde{\Psi}(t)\rangle$ in (4.1.11) now becomes

$$i\hbar\frac{d}{dt}\big|\widetilde{\Psi}(t)\big\rangle \;=\; \lambda\widetilde{\delta H}(t)\big|\widetilde{\Psi}(t)\big\rangle . \tag{4.2.2}$$

As we did in time-independent perturbation theory we start by expanding $\big|\widetilde{\Psi}(t)\big\rangle$ in powers of the parameter λ:

$$\big|\widetilde{\Psi}(t)\big\rangle \;=\; \big|\widetilde{\Psi}^{(0)}(t)\big\rangle \;+\lambda\big|\widetilde{\Psi}^{(1)}(t)\big\rangle \;+\lambda^2\big|\widetilde{\Psi}^{(2)}(t)\big\rangle \;+\mathcal{O}\left(\lambda^3\right) . \tag{4.2.3}$$

We now insert this into both sides of the Schrödinger equation (4.2.2), and using ∂_t for time derivatives, we find

$$\begin{aligned} &i\hbar\partial_t\big|\widetilde{\Psi}^{(0)}(t)\big\rangle + \lambda\, i\hbar\partial_t\big|\widetilde{\Psi}^{(1)}(t)\big\rangle + \lambda^2\, i\hbar\partial_t\big|\widetilde{\Psi}^{(2)}(t)\big\rangle + \lambda^3\, i\hbar\partial_t\big|\widetilde{\Psi}^{(2)}(t)\big\rangle + \mathcal{O}\left(\lambda^4\right) \\ &\quad = \lambda\,\widetilde{\delta H}\big|\widetilde{\Psi}^{(0)}(t)\big\rangle + \lambda^2\,\widetilde{\delta H}\,\big|\widetilde{\Psi}^{(1)}(t)\big\rangle + \lambda^3\,\widetilde{\delta H}\,\big|\widetilde{\Psi}^{(2)}(t)\big\rangle + \mathcal{O}\left(\lambda^4\right)\,. \end{aligned} \tag{4.2.4}$$

The coefficient of each power of λ must vanish, giving us

$$\begin{aligned} i\hbar\partial_t\big|\widetilde{\Psi}^{(0)}(t)\big\rangle &= 0\,, \\ i\hbar\partial_t\big|\widetilde{\Psi}^{(1)}(t)\big\rangle &= \widetilde{\delta H}\big|\widetilde{\Psi}^{(0)}(t)\big\rangle\,, \\ i\hbar\partial_t\big|\widetilde{\Psi}^{(2)}(t)\big\rangle &= \widetilde{\delta H}\big|\widetilde{\Psi}^{(1)}(t)\big\rangle\,, \\ \vdots \qquad &= \qquad \vdots \\ i\hbar\partial_t\big|\widetilde{\Psi}^{(n+1)}(t)\big\rangle &= \widetilde{\delta H}\big|\widetilde{\Psi}^{(n)}(t)\big\rangle\,. \end{aligned} \tag{4.2.5}$$

The origin of the pattern is clear. Since the Schrödinger equation has an explicit λ multiplying the right-hand side, the time derivative of the n-th component is coupled to the $\widetilde{\delta H}$ perturbation acting on the $(n-1)$-th component.

Let us consider the initial condition in detail. We will assume that the perturbation turns on at $t = 0$, so that the initial condition is given in terms of $|\Psi(0)\rangle$. Since our Schrödinger equation is in terms of $|\widetilde{\Psi}(t)\rangle$ we use the relation ((4.1.8)) between them to conclude that both tilde and un-tilde wavefunctions are equal at $t = 0$:

$$|\widetilde{\Psi}(0)\rangle \;=\; |\Psi(0)\rangle\,. \tag{4.2.6}$$

Given this, the expansion (4.2.3) evaluated at $t = 0$ implies that:

$$\big|\widetilde{\Psi}(0)\big\rangle \;=\; |\Psi(0)\rangle \;=\; \big|\widetilde{\Psi}^{(0)}(0)\big\rangle \;+\lambda\big|\widetilde{\Psi}^{(1)}(0)\big\rangle \;+\lambda^2\big|\widetilde{\Psi}^{(2)}(0)\big\rangle \;+\mathcal{O}\left(\lambda^3\right)\,. \tag{4.2.7}$$

This must be viewed, again, as an equation that holds for all values of λ. As a result, the coefficient of each power of λ must vanish and we have

$$\begin{aligned} \big|\widetilde{\Psi}^{(0)}(0)\big\rangle &= \big|\Psi(0)\big\rangle\,, \\ \big|\widetilde{\Psi}^{(n)}(0)\big\rangle &= 0\,, \qquad n = 1, 2, 3 \ldots\,. \end{aligned} \tag{4.2.8}$$

These are the relevant initial conditions.

Consider now the first equation in (4.2.5). It states that $\big|\widetilde{\Psi}^{(0)}(t)\big\rangle$ is time independent. This is reasonable: if the perturbation vanishes, this is the only equation we get and we should expect $\big|\widetilde{\Psi}(t)\big\rangle$ constant. Using the time-independence of $\big|\widetilde{\Psi}^{(0)}(t)\big\rangle$ and the initial condition we have

$$\big|\widetilde{\Psi}^{(0)}(t)\big\rangle = \big|\widetilde{\Psi}^{(0)}(0)\big\rangle = \big|\Psi(0)\big\rangle\,, \tag{4.2.9}$$

and we have solved the first equation completely:

$$\boxed{\big|\widetilde{\Psi}^{(0)}\big\rangle = \big|\Psi(0)\big\rangle\,.} \tag{4.2.10}$$

Using this result, the $\mathcal{O}(\lambda)$ equation reads:

$$i\hbar\partial_t\big|\widetilde{\Psi}^{(1)}(t)\big\rangle = \widetilde{\delta H}\big|\widetilde{\Psi}^{(0)}(t)\big\rangle = \widetilde{\delta H}(t)\big|\Psi(0)\big\rangle\,. \tag{4.2.11}$$

The solution can be written as an integral:

$$\boxed{\big|\widetilde{\Psi}^{(1)}(t)\big\rangle = \int_0^t \frac{\widetilde{\delta H}(t')}{i\hbar}\big|\Psi(0)\big\rangle\,dt'\,.} \tag{4.2.12}$$

Note that by setting the lower limit of integration at $t=0$ we have implemented correctly the initial condition $|\widetilde{\Psi}^{(1)}(0)\rangle = 0$. The next equation, of order λ^2 reads:

$$i\hbar\partial_t\big|\widetilde{\Psi}^{(2)}(t)\big\rangle = \widetilde{\delta H}\big|\widetilde{\Psi}^{(1)}(t)\big\rangle\,, \tag{4.2.13}$$

and its solution is

$$\big|\widetilde{\Psi}^{(2)}(t)\big\rangle = \int_0^t \frac{\widetilde{\delta H}(t')}{i\hbar}\big|\widetilde{\Psi}^{(1)}(t')\big\rangle\,dt'\,, \tag{4.2.14}$$

consistent with the initial condition. Using our previous result to write $\big|\widetilde{\Psi}^{(1)}(t')\big\rangle$ we now have an iterated integral expression:

$$\boxed{\big|\widetilde{\Psi}^{(2)}(t)\big\rangle = \int_0^t \frac{\widetilde{\delta H}(t')}{i\hbar}dt' \int_0^{t'} \frac{\widetilde{\delta H}(t'')}{i\hbar}\big|\Psi(0)\big\rangle dt''\,.} \tag{4.2.15}$$

It should be clear from this discussion how to write the iterated integral expression for $\big|\widetilde{\Psi}^{(k)}(t)\big\rangle$, with $k>2$. The solution, setting $\lambda=1$ and summarizing is then

$$\big|\Psi(t)\big\rangle = \exp\Big(-\frac{iH^{(0)}t}{\hbar}\Big)\left(|\Psi(0)\rangle + |\widetilde{\Psi}^{(1)}(t)\rangle + \ |\widetilde{\Psi}^{(2)}(t)\rangle + \cdots\right) \tag{4.2.16}$$

Let us use our perturbation theory to calculate the probability $P_{m\leftarrow n}(t)$ to transition from $|n\rangle$ at $t=0$ to $|m\rangle$, with $m\neq n$, at time t, under the effect of the perturbation. By definition

$$P_{m\leftarrow n}(t) \ = \ \big|\langle m|\Psi(t)\rangle\big|^2\,. \tag{4.2.17}$$

Using the tilde wavefunction, for which we know how to write the perturbation, we have

$$P_{m\leftarrow n}(t) \ = \ \big|\langle m|e^{-iH^{(0)}t/\hbar}\big|\widetilde{\Psi}(t)\big\rangle\big|^2 \ = \ \big|\langle m|\widetilde{\Psi}(t)\rangle\big|^2\,, \tag{4.2.18}$$

since the phase that arises from the action on the bra vanishes upon the calculation of the norm squared. Now using the perturbation expression for $|\widetilde{\Psi}(t)\rangle$ (setting $\lambda = 1$) we have

$$P_{m\leftarrow n}(t) = \left|\langle m|\left(\left|\Psi^{(0)}\right\rangle + \left|\widetilde{\Psi}^{(1)}(t)\right\rangle + \left|\widetilde{\Psi}^{(2)}(t)\right\rangle + \dots\right)\right|^2 . \tag{4.2.19}$$

Since we are told that $|\Psi(0)\rangle = |n\rangle$ and $|n\rangle$ is orthogonal to $|m\rangle$ we find

$$P_{m\leftarrow n}(t) = \left|\langle m|\widetilde{\Psi}^{(1)}(t)\rangle + \langle m|\widetilde{\Psi}^{(2)}(t)\rangle + \dots\right|^2 . \tag{4.2.20}$$

To first order in perturbation theory we only keep the first term in the sum and using our result for $|\widetilde{\Psi}^{(1)}(t)\rangle$ we find

$$P^{(1)}_{m\leftarrow n}(t) \;=\; \left|\langle m|\int_0^t \frac{\widetilde{\delta H}(t')}{i\hbar}|n\rangle\, dt'\right|^2 \;=\; \left|\int_0^t \frac{\langle m|\widetilde{\delta H}(t')|n\rangle}{i\hbar}\, dt'\;\right|^2 . \tag{4.2.21}$$

Recalling the relation between the matrix elements of $\widetilde{\delta H}$ and those of δH we finally have our result for the transition probability to first order in perturbation theory:

$$\boxed{P^{(1)}_{m\leftarrow n}(t) \;=\; \left|\int_0^t e^{i\omega_{mn}t'}\frac{\delta H_{mn}(t')}{i\hbar}dt'\right|^2 .} \tag{4.2.22}$$

This is a key result and will be very useful in the applications we will consider.

Exercise: Prove the remarkable equality of transition probabilities

$$\boxed{P^{(1)}_{m\leftarrow n}(t) \;=\; P^{(1)}_{n\leftarrow m}(t)\,,} \tag{4.2.23}$$

valid to first order in perturbation theory.

It will also be useful to have our results in terms of the time-dependent coefficients $c_n(t)$ introduced earlier through the expansion

$$\left|\widetilde{\Psi}(t)\right\rangle = \sum_n c_n(t)|n\rangle\,. \tag{4.2.24}$$

Since $\left|\Psi(0)\right\rangle = \left|\widetilde{\Psi}(0)\right\rangle$ the initial condition reads

$$\left|\Psi(0)\right\rangle \;=\; \sum_n c_n(0)|n\rangle \;=\; \left|\widetilde{\Psi}^{(0)}(0)\right\rangle, \tag{4.2.25}$$

where we also used (4.2.9). In this notation, the $c_n(t)$ functions also have a λ expansion, because we write

$$\left|\widetilde{\Psi}^{(k)}(t)\right\rangle = \sum_n c_n^{(k)}(t)|n\rangle\,, \quad k = 0, 1, 2, \dots \tag{4.2.26}$$

and therefore the earlier relation

$$\big|\widetilde{\Psi}(t)\big\rangle \;=\; \big|\widetilde{\Psi}^{(0)}(t)\big\rangle \;+\lambda\big|\widetilde{\Psi}^{(1)}(t)\big\rangle \;+\lambda^2\big|\widetilde{\Psi}^{(2)}(t)\big\rangle \;+\mathcal{O}\left(\lambda^3\right)\,. \tag{4.2.27}$$

now gives

$$c_n(t) \;=\; c_n^{(0)}(t)+\lambda c_n^{(1)}(t)+\lambda^2 c_n^{(2)}(t)+\ldots \tag{4.2.28}$$

Since $|\widetilde{\Psi}^{(0)}(t)\rangle$ is in fact constant we have

$$c_n^{(0)}(t)=c_n^{(0)}(0)=c_n(0)\,, \tag{4.2.29}$$

where we used (4.2.25). The other initial conditions given earlier in (4.2.8) imply that

$$c_n^{(k)}(0) \;=\; 0\,,\qquad k=1,2,3\ldots\,. \tag{4.2.30}$$

Therefore, using our result (4.2.12) for $\big|\widetilde{\Psi}^{(1)}(t)\big\rangle$ we have

$$\big|\widetilde{\Psi}^{(1)}(t)\big\rangle=\sum_n c_n^{(1)}(t)|n\rangle=\int_0^t\frac{\widetilde{\delta H}(t')}{i\hbar}dt'\,\sum_n c_n(0)|n\rangle\,, \tag{4.2.31}$$

and as a result,

$$c_m^{(1)}(t)\equiv\langle m\,\big|\widetilde{\Psi}^{(1)}(t)\big\rangle=\sum_n\int_0^t\frac{\langle m|\widetilde{\delta H}(t')|n\rangle}{i\hbar}c_n(0)\,dt'\,. \tag{4.2.32}$$

We therefore have

$$\boxed{\;c_m^{(1)}(t) \;=\; \sum_n\int_0^t dt'\,e^{i\omega_{mn}t'}\,\frac{\delta H_{mn}(t')}{i\hbar}\,c_n(0)\,.\;} \tag{4.2.33}$$

The probability $P_m(t)$ to be found in the state $|m\rangle$ at time t is

$$P_m(t) \;=\; |\langle m|\Psi(t)\rangle|^2 \;=\; \Big|\langle m|\widetilde{\Psi}(t)\rangle\Big|^2 \;=|c_m(t)|^2\,. \tag{4.2.34}$$

To first order in perturbation theory the answer would be (with $\lambda=1$)

$$\begin{aligned}P_m^{(1)}(t) \;&=\big|c_m(0)+c_m^{(1)}(t)\big|^2\\ &=\big|c_m(0)\big|^2+c_m(0)^*c_m^{(1)}(t)+c_m^{(1)}(t)^*c_m(0)+\mathcal{O}(\delta H^2)\,.\end{aligned} \tag{4.2.35}$$

Note that the $|c_m^{(1)}(t)|^2$ term cannot be kept to this order of approximation, since it is of the same order as contributions that would arise from $c_m^{(2)}(t)$.

4.2.1 Example NMR

The Hamiltonian for a particle with a magnetic moment inside a magnetic field can be written in the form

$$H = \boldsymbol{\omega} \cdot \mathbf{S}\,, \tag{4.2.36}$$

where $\mathbf{S}$ is the spin operator and $\boldsymbol{\omega}$ is precession angular velocity vector, itself a function of the magnetic field. Note that the Hamiltonian has properly units of energy ($\omega\hbar$). Let us take the unperturbed Hamiltonian to be

$$H^{(0)} = \omega_0 S_z = \tfrac{\hbar}{2}\,\omega_0 \sigma_z\,. \tag{4.2.37}$$

For NMR applications one has $\omega_0 \approx 500$ Hz and this represents the physics of a magnetic field along the z axis. Let us now consider some possible perturbations.

Case 1: Time independent perturbation Let us consider adding at $t = 0$ a constant perturbation associated with an additional small uniform magnetic field along the x axis:

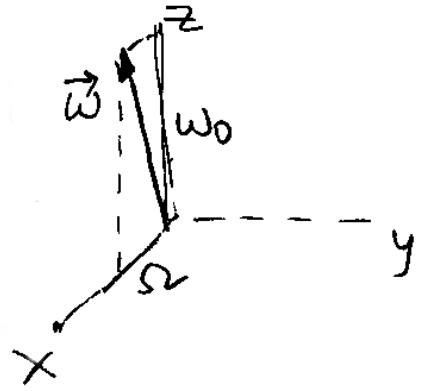
$$H = H^{(0)} + \delta H\,, \quad \text{with} \quad \delta H = \Omega S_x\,, \tag{4.2.38}$$

For this to be a small perturbation we will take

$$\Omega \ll \omega_0\,. \tag{4.2.39}$$

Hence, for the full Hamiltonian H we have $\boldsymbol{\omega} = (\Omega, 0, \omega_0)$

$$H = \underbrace{(\Omega, 0, \omega_0)}_{\boldsymbol{\omega}} \cdot (S_x, S_y, S_z) \tag{4.2.40}$$



The problem is simple enough that an exact solution is possible. The perturbed Hamiltonian H has energy eigenstates $|\mathbf{n};\pm\rangle$, spin states that point with $\mathbf{n} = \frac{\boldsymbol{\omega}}{|\boldsymbol{\omega}|}$ with energies $\pm\frac{\hbar}{2}|\omega|$. These eigenstates could be recovered using time-independent non-degenerate perturbation theory using Ω/ω_0 as a small parameter and starting with the eigenstates $|\pm\rangle$ of $H^{(0)}$.

In *time-dependent* perturbation theory we obtain the time-dependent evolution of initial states as they are affected by the perturbation. Recalling (4.2.12) we have

$$\big|\widetilde{\Psi}^{(1)}(t)\big\rangle = \int_0^t \frac{\widetilde{\delta H}(t')}{i\hbar}\big|\Psi(0)\big\rangle dt' \tag{4.2.41}$$

The calculation of $\widetilde{\delta H}$ requires a bit of computation. One quickly finds that

$$\widetilde{\delta H}(t) = \exp\left[i\omega_0 t\frac{\sigma_z}{2}\right]\Omega\hat{S}_x\exp\left[-i\omega_0 t\frac{\sigma_z}{2}\right] = \Omega\left(\hat{S}_x\cos\omega_0 t - \hat{S}_y\sin\omega_0 t\right)\,. \tag{4.2.42}$$

As a result we set:

$$\begin{aligned}\big|\widetilde{\Psi}^{(1)}(t)\big\rangle &= \frac{\Omega}{i\hbar}\int_0^t\left(\hat{S}_x\cos\omega_0 t' - \hat{S}_y\sin\omega_0 t'\right)\big|\Psi(0)\big\rangle dt' \\ &= \frac{1}{i\hbar}\frac{\Omega}{\omega_0}\left[\hat{S}_x\sin\omega_0 t + \big(\cos(\omega_0 t') - 1\big)\hat{S}_y\right]\big|\Psi(0)\big\rangle\,.\end{aligned} \tag{4.2.43}$$

As expected, the result is first order in the small parameter Ω/ω_0. Following (4.2.16) the time-dependent state is, to first approximation

$$\begin{aligned}\big|\Psi(t)\big\rangle \;=\; &\exp\left[-i\omega_0 t\frac{\sigma_z}{2}\right]\left(1 + \frac{1}{i\hbar}\frac{\Omega}{\omega_0}\left[\hat{S}_x\sin\omega_0 t + \big(\cos(\omega_0 t') - 1\big)\hat{S}_y\right]\right)|\Psi(0)\rangle \\ &+ \mathcal{O}((\Omega/\omega_0)^2)\,.\end{aligned} \tag{4.2.44}$$

Physically the solution is clear. The original spin state $\big|\Psi(0)\big\rangle$ precesses about the direction of $\boldsymbol{\omega}$ with angular velocity ω.

Case 2: Time dependent perturbation. Suppose that to the original Hamiltonian we add the effect of a rotating magnetic field, rotating with the same angular velocity ω_0 that corresponds to the Larmor frequency of the original Hamiltonian:

$$\delta H(t) = \Omega\left(\hat{S}_x\cos\omega_0 t + \hat{S}_y\sin\omega_0 t\right)\,. \tag{4.2.45}$$

To compute the perturbation $\widetilde{\delta H}$ we can use (4.2.42) with t replaced by $-t$ so that the right-hand side of this equation is proportional to δH:

$$\exp\left[-i\omega_0 t\frac{\sigma_z}{2}\right]\Omega\hat{S}_x\exp\left[i\omega_0 t\frac{\sigma_z}{2}\right] = \Omega\left(\hat{S}_x\cos\omega_0 t + \hat{S}_y\sin\omega_0 t\right)\,. \tag{4.2.46}$$

Moving the exponentials on the left-hand side to the right-hand side we find

$$\Omega\hat{S}_x = \exp\left[i\omega_0 t\frac{\sigma_z}{2}\right]\Omega\left(\hat{S}_x\cos\omega_0 t + \hat{S}_y\sin\omega_0 t\right)\exp\left[-i\omega_0 t\frac{\sigma_z}{2}\right]\,. \tag{4.2.47}$$

The right-hand side is, by definition, $\widetilde{\delta H}$. Thus we have shown that

$$\widetilde{\delta H}(t) = \Omega\hat{S}_x\,, \tag{4.2.48}$$

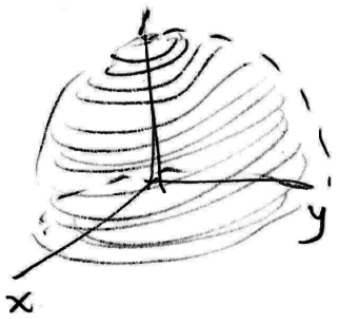
is in fact a time-independent Hamiltonian. This means that the Schrödinger equation for $\big|\widetilde{\Psi}\big\rangle$ is immediately solved

$$\big|\widetilde{\Psi}(t)\big\rangle \;=\; \exp\left[-i\frac{\widetilde{\delta H}t}{\hbar}\right]\big|\widetilde{\Psi}(0)\big\rangle \;=\; \exp\left[-i\frac{\Omega\hat{S}_x\,t}{\hbar}\right]\big|\Psi(0)\big\rangle\,. \tag{4.2.49}$$

The complete and exact answer is therefore

$$\boxed{\left|\Psi(t)\right\rangle = \exp\Big[-\frac{iH^{(0)}t}{\hbar}\Big]\left|\widetilde{\Psi}(t)\right\rangle = \exp\left[-i\omega_0 t\frac{\sigma_z}{2}\right]\exp\left[-i\Omega t\frac{\sigma_x}{2}\right]\left|\Psi(0)\right\rangle .} \tag{4.2.50}$$

This is a much more non trivial motion! A spin originally aligned along $\hat{z}$ will spiral into the x, y plane with angular velocity Ω.



4.3 Fermi's Golden Rule

Let us now consider transitions where the initial state is part of a discrete spectrum but the final state is part of a continuum. The ionization of an atom is perhaps the most familiar example: the initial state may be one of the discrete bound states of the atom while the final state includes a free electron a momentum eigenstate that is part of a continuum of non-normalizable states.

As we will see, while the probability of transition between discrete states exhibits periodic dependence in time, if the final state is part of a continuum an integral over final states is needed and the result is a transition probability *linear* in time. To such probability function we will be able to associate a transition *rate*. The final answer for the transition rate is given by Fermi's Golden Rule.

We will consider two different cases in full detail:

1. Constant perturbations. In this case the perturbation, called V turns on at $t = 0$ but it is otherwise time independent:

$$H \;=\; \begin{cases} H^{(0)}\,, & \text{for } \; t \le 0\,, \\ H^{(0)} + V & \text{for } \; t > 0\,. \end{cases} \tag{4.3.1}$$

   This situation is relevant for the phenomenon of auto-ionization, where an internal transition in the atom is accompanied by the ejection of an electron.

2. Harmonic perturbations. In this case the time dependence of the perturbation δH is periodic, namely,

$$H(t) \;=\; H^{(0)} + \delta H(t)\,, \tag{4.3.2}$$

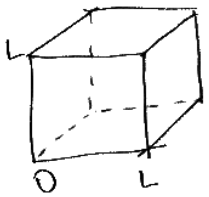
with

$$\delta H(t) \;=\; \begin{cases} 0\,, & \text{for } \; t \leq 0\,, \\ 2H' \cos\omega t\,, & \text{for } \; t > 0\,. \end{cases} \tag{4.3.3}$$

Note the factor of two entering the definition of δH in terms of the time independent H'. This situation is relevant to the interaction of electromagnetic fields with atoms.

Before starting with the analysis of these two cases let us consider the way to deal with continuum states, as the final states in the transition will belong to a continuum. The fact is that we need to be able to count the states in the continuuum, so we will replace infinite space by a very large cubic box of side length L and we will impose periodic boundary conditions on the wavefunctions. The result will be a discrete spectrum where the separation between the states can be made arbitrarily small, thus simulating accurately a continuum in the limit $L \to \infty$. If the states are energetic enough and the potential is short range, momentum eigenstates are a good representation of the continuum.

To count states use a large box, which can be taken to be a cube of side L:



We call L a regulator as it allows us to deal with infinite quantities (like the volume of space or the number of continuum states). At the end of our calculations the value of L must drop out. This is a consistency check. The momentum eigenstates $\psi($**x** take the form

$$\psi(\mathbf{x}) = \frac{1}{\sqrt{L^3}} e^{ik_x x} e^{ik_y y} e^{ik_z z}\,, \tag{4.3.4}$$

with constant $\mathbf{k} = (k_x, k_y, k_z)$. It is clear that the states are normalized correctly

$$\int_{\rm box} |\psi(\mathbf{x})|^2 d^3x = \frac{1}{L^3} \int d^3x = 1\,. \tag{4.3.5}$$

The $k's$ are quantized by the periodicity condition on the wavefunction:

$$\psi(x+L,y,z) \;=\; \psi(x,y+L,z) \;=\; \psi(x,y,z+L) \;=\; \psi(x,y,z)\,. \tag{4.3.6}$$

The quantization gives

$$\begin{aligned} k_x L = 2\pi n_x \quad &\to \quad L dk_x = 2\pi dn_x\,, \\ k_y L = 2\pi n_y \quad &\to \quad L dk_y = 2\pi dn_y\,, \\ k_z L = 2\pi n_z \quad &\to \quad L dk_z = 2\pi dn_z\,. \end{aligned} \tag{4.3.7}$$

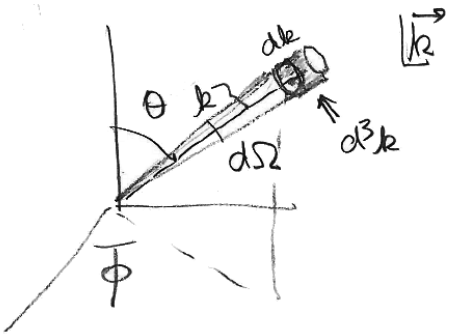
Define ΔN as the total number of states within the little cubic volume element d^3k. It follows from (4.3.7) that we have

$$\Delta N \equiv dn_x\, dn_y\, dn_z \;=\; \left(\frac{L}{2\pi}\right)^3 d^3k\,. \tag{4.3.8}$$

Note that ΔN only depends on d^3k and not on $\mathbf{k}$ itself: the density of states is constant in momentum space.

Now let d^3k be a volume element determined in spherical coordinates k, θ, ϕ and by ranges $dk, d\theta, d\phi$. Therefore

$$d^3k \;=\; k^2 dk\, \sin\theta d\theta\, d\phi \;=\; k^2 dk\, d\Omega \tag{4.3.9}$$



We now want to express the density of states as a function of energy. For this we take differentials of the relation between the wavenumber k and the energy E:

$$E = \frac{\hbar^2 k^2}{2m} \qquad \to \qquad k dk = \frac{m}{\hbar^2}\, dE\,. \tag{4.3.10}$$

Back in (4.3.9) we have

$$d^3k \;=\; k\, \frac{m}{\hbar^2}\, dE\, d\Omega\,, \tag{4.3.11}$$

hence

$$\Delta N \;=\; \left(\frac{L}{2\pi}\right)^3 k\, \frac{m}{\hbar^2}\, d\Omega\, dE\,. \tag{4.3.12}$$

We now equate

$$\Delta N \;=\; \rho(E) dE\,, \tag{4.3.13}$$

where $\rho(E)$ is a *density* of states, more precisely, it is the number of states per unit energy at around energy E and with momentum pointing within the solid angle $d\Omega$. The last two equations determine for us this density:

$$\boxed{\rho(E) \;=\; \frac{L^3}{8\pi^3}\, \frac{m}{\hbar^2}\, k\, d\Omega\,.} \tag{4.3.14}$$

With a very large box, a sum over states can be replaced by an integral as follows

$$\sum_{\text{states}} \cdots \;\to\; \int \cdots \rho(E) dE \tag{4.3.15}$$

where the dots denote an arbitrary function of the momenta $\mathbf{k}$ of the states.

4.3.1 Constant transitions.

The Hamiltonian, as given in (4.3.1) takes the form

$$H = \begin{cases} H^{(0)} & \text{for } t \leq 0 \\ H^{(0)} + V & \text{for } t > 0\,. \end{cases} \tag{4.3.16}$$

We thus identify $\delta H(t) = V$ for $t \geq 0$. Recalling the formula (4.2.33) for transition amplitudes to first order in perturbation theory we have

$$c_m^{(1)}(t) = \sum_n \int_0^t dt' e^{i\omega_{mn}t'} \frac{V_{mn}}{i\hbar} c_n(0)\,. \tag{4.3.17}$$

To represent an initial state i at $= 0$ we take $c_n(0) = \delta_{n,i}$. For a transition to a final state f at time t_0 we set $m = f$ and we have an integral that is easily performed:

$$c_f^{(1)}(t_0) = \frac{1}{i\hbar}\int_0^{t_0} V_{fi}\, e^{i\omega_{fi}\,t'} dt' = \frac{V_{fi}}{i\hbar}\ \frac{e^{i\omega_{fi}\,t'}}{i\omega_{fi}}\bigg|_0^{t_0} \tag{4.3.18}$$

Evaluating the limits and simplifying

$$c_f^{(1)}(t_0) = \frac{V_{fi}}{E_f - E_i}\left(1 - e^{i\omega_{fi}\,t^0}\right) = \frac{V_{fi}\, e^{i\omega_{fi}t_0/2}}{E_f - E_i}\,(-2i)\sin\left(\frac{\omega_{fi}\,t^0}{2}\right)\,. \tag{4.3.19}$$

The transition probability to go from i at $t = 0$ to f at $t = t_0$ is then $|c_f^{(1)}(t_0)|^2$ and is therefore

$$\boxed{P_{f\leftarrow i}(t_0) = |V_{fi}|^2 \frac{4\sin^2\left(\frac{\omega_{fi}\,t_0}{2}\right)}{(E_f - E_i)^2}\ .} \tag{4.3.20}$$

This first order result in perturbation theory is expected to be accurate at time t_0 if $P_{f\leftarrow i}(t_0) \ll 1$. Certainly a large transition probability at first order could not be trusted and would require examination of higher orders.

To understand the main features of the result for the transition probability we examine how it behaves for different values of the final energy E_f. If $E_f \neq E_i$ the transition is said to be energy non-conserving. Of course, energy is conserved overall, as it would be supplied by the perturbation. If $E_f = E_i$ we have an energy conserving transition. Both are possible and let us consider them in turn.

1. $E_f \neq E_i$. In this case the transition probability $P_{f\leftarrow i}(t_0)$ as a function of t_0 is shown in Figure 4.2. The behavior is oscillatory with frequency $|\omega_{fi}$. If the amplitude of the oscillation is much less than one

$$\frac{4|V_{fi}|^2}{(E_f - E_i)^2} \ll 1 \tag{4.3.21}$$

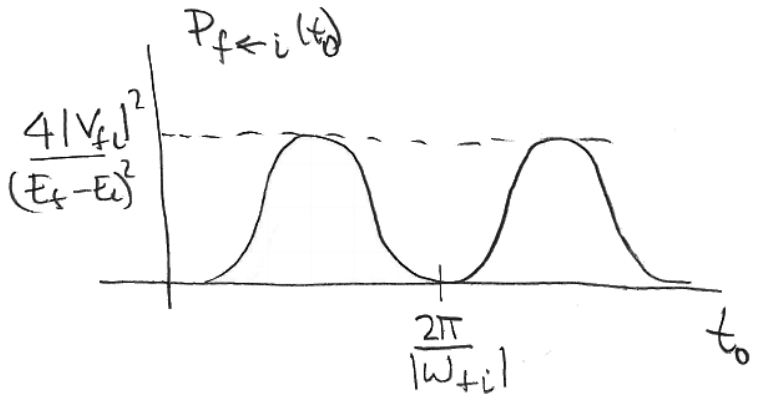


Figure 4.2: The transition probability as a function of time for constant perturbations.

then this first order transition probability $P_{f\leftarrow i}(t_0)$ is accurate for all times t_0 as it is always small. The amplitude is suppressed as $|E_f - E_i|$ grows, due to the factor in the denominator. This indicates that the larger the energy 'violation' the smaller the probability of transition. This is happening because a perturbation that turns on and then remains constant is not an efficient supply of energy.

2. $E_f \to E_i$. In this limit ω_{fi} approaches zero and therefore

$$\sin^2\left(\frac{\omega_{fi}\, t_0}{2}\right) \;\simeq\; \frac{(E_f - E_i)^2}{4\hbar^2}\, t_0^2\,. \tag{4.3.22}$$

It follows from (4.3.20) that

$$\lim_{E_f\to E_i} P_{f\leftarrow i}(t_0) \;=\; \frac{|V_{fi}|^2}{\hbar^2} t_0^2\,. \tag{4.3.23}$$

The probability for an energy-conserving transition grows quadratically in time, and does so without bound! This result, however, can only be trusted for small enough t_0 such that $P_{f\leftarrow i}(t_0) \ll 1$.

Note that a quadratic growth of $P_{f\leftarrow i}$ is also visible in the energy non-conserving $E_f \neq E_i$ case for very small times t_0. Indeed, (4.3.20) leads again to $\lim_{t_0\to 0} P_{f\leftarrow i}(t_0) = |V_{fi}|^2 t_0^2/\hbar^2$, while $E_f \neq E_i$. This behavior can be noted near the origin in Figure 4.2.

Our next step is to integrate the transition probability over the now discretized continuum of final states. Remarkably, upon integration the oscillatory and quadratic behaviors of the transition probability as a function of time will conspire to create a linear behavior!

The sum of transition probabilities over final states is approximated by an integral, as explained in (4.3.15). We thus have

$$\sum_f P_{f\leftarrow i}(t_0) = \int P_{f\leftarrow i}(t_0)\rho(E_f)dE_f = 4\int |V_{fi}|^2 \frac{\sin^2\left(\frac{\omega_{fi}\, t_0}{2}\right)}{(E_f - E_i)^2}\rho(E_f)dE_f\,. \tag{4.3.24}$$

We have noted that $P_{f\leftarrow i}$ in the above integrand is suppressed as $|E_f - E_i|$ becomes large. We therefore expect that the bulk of the contribution to the integral will occur for a narrow range ΔE_f of E_f near E_i. Let us assume now that $|V_{fi}|^2$ and $\rho(E_f)$ are slow varying and therefore approximately constant over the narrow interval E_f (we will re-examine this assumption below). If this is the case we can evaluate them for E_f set equal to E_i and take them out of the integrand to find

$$\sum_f P_{f\leftarrow i}(t_0) = \frac{4|V_{fi}|^2}{\hbar^2}\rho(E_f = E_i)\cdot I(t_0)\,, \tag{4.3.25}$$

where the integral $I(t_0)$ is given by

$$I(t_0) \;\equiv\; \int \frac{1}{\omega_{fi}^2}\sin^2\left(\frac{\omega_{fi}\,t_0}{2}\right)\,dE_f = \hbar\int \sin^2\left(\frac{\omega_{fi}\,t_0}{2}\right)\,\frac{d\omega_{fi}}{\omega_{fi}^2}\,. \tag{4.3.26}$$

As it stands, the integral extends from minus infinity to plus infinity. It is useful to plot the final integrand for $I(t_0)$ as a function of the integration variable ω_{fi}. The result is shown in Figure 4.3 and exhibits a main central lobe followed by symmetrically arranged lobes of decreasing amplitude. The lobes are separated by zeroes occurring for $\omega_{fi} = 2\pi k/t_0$, with k integer. Note that for

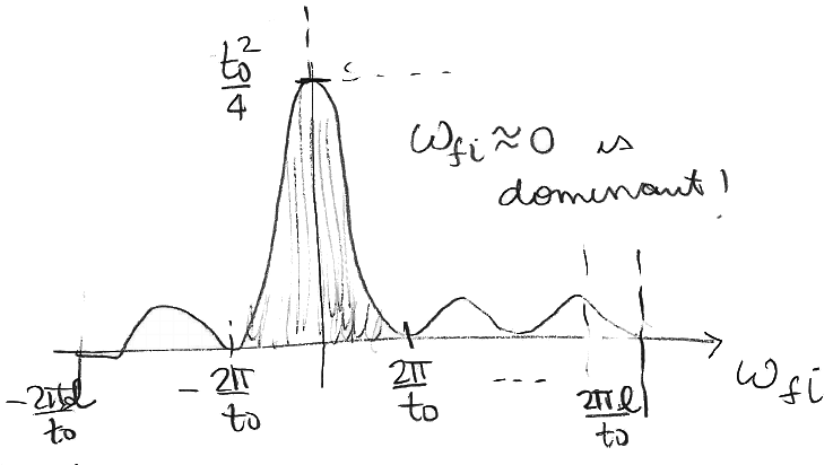


Figure 4.3: Plot of $\frac{1}{\omega_{fi}^2}\sin^2\left(\frac{\omega_{fi}\,t_0}{2}\right)$, the integrand of I.

The largest contribution to $I(t_0)$ arises from the main lobe

$$-\frac{2\pi}{t_0} \;<\; \omega_{fi} \;<\; \frac{2\pi}{t_0}\,. \tag{4.3.27}$$

In terms of energies this corresponds to the range

$$E_i - \frac{2\pi\hbar}{t_0} \;<\; E_f \;<\; E_i + \frac{2\pi\hbar}{t_0}\,. \tag{4.3.28}$$

We need this range to be a narrow, thus $\mathbf{t_0}$ **must be sufficiently large**. The narrowness is required to justify our taking of the density of states $\rho(E)$ and the matrix element $|V_{fi}|^2$ out of the integral. If we want to include more lobes this is can be made consistent with a narrow range of energies by making t_0 larger.

The linear dependence of $I(t_0)$ as a function of t_0 is intuitively appreciated by noticing that the height of the main lobe is proportional to t_0^2 and its width is proportional to $1/t_0$. In fact, the linear dependence is a simple mathematical fact made manifest by a change of variables. Letting

$$u = \frac{\omega_{fi} t_0}{2} \implies du = \frac{t_0}{2} d\omega_{fi} \,, \tag{4.3.29}$$

so that

$$I(t_0) \;=\; \frac{2\hbar}{t_0} \int_{-\infty}^{\infty} \frac{\sin^2 u}{u^2 \cdot \frac{4}{t_0^2}} \;=\; \frac{\hbar t_0}{2} \int_{-\infty}^{\infty} \frac{\sin^2 u}{u^2} \,, \tag{4.3.30}$$

making the linear dependence in t_0 manifest. The remaining integral evaluates to π and we thus get

$$I(t_0) \;=\; \tfrac{\pi}{2}\, \hbar t_0 \ . \tag{4.3.31}$$

Had restricted the integral to the main lobe, concerned that the density of states and matrix elements would vary over larger ranges, we would have gotten 90% of the total contribution. Including the next two lobes, one to the left and one to the right, brings the result up to 95% of the total contribution. By the time we include ten or more lobes on each side we are getting 99% of the answer. For sufficiently large t_0 is is still a narrow range.

Having determined the value of the integral $I(t_0)$ we can substitute back into our expression for the transition probability (4.3.26). Replacing t_0 by t

$$\sum_k P_{k\leftarrow i}(t) = \frac{4|V_{fi}|^2}{\hbar^2} \rho(E_f)\, \frac{\pi}{2}\, \hbar t \;=\; \frac{2\pi}{\hbar} |V_{fi}|^2 \rho(E_f)\, t \,. \tag{4.3.32}$$

This holds, as discussed before, for sufficiently large t. Of course t cannot be too large as it would make the transition probability large and unreliable. The linear dependence of the transition probability implies we can define a transition rate w, or probability of transition per unit time, by dividing the transition probability by t:

$$w \equiv \frac{1}{t} \sum_f P_{f\leftarrow i}(t) \,. \tag{4.3.33}$$

This finally gives us Fermi's golden rule for constant perturbations:

$$\boxed{\text{Fermi's golden rule:} \quad w \;=\; \frac{2\pi}{\hbar} |V_{fi}|^2 \rho(E_f) \,, \quad E_f = E_i \,.} \tag{4.3.34}$$

Not only is the density of states evaluated at the energy E_i, the matrix element V_{fi} is also evaluated at the energy E_i and other observables of the final state, like the momentum. In

this version of the golden rule the integration over final states has been performed. The units are manifestly right: $|V_{fi}|^2$ has units of energy squared, ρ has units of one over energy, and with an $\hbar$ in the denominator the whole expression has units of one over time, as appropriate for a rate. We can also see that the dependence of w on the size-of-the-box regulator L disappears: The matrix element

$$V_{fi} = \langle f|V|i\rangle \sim L^{-3/2}\,, \tag{4.3.35}$$

because the final state wavefunction has such dependence (see (4.3.4)). Then the L dependence in $|V_{fi}|^2 \sim L^{-3}$ cancels with the L dependence of the density of states $\rho \sim L^3$, noted in (4.3.14).

Let us summarize the approximations used to derive the golden rule. We have two conditions that must hold simultaneously:

1. We assumed that t_0 is large enough so that the energy range

$$E_i - k\,\frac{2\pi\hbar}{t_0} \;<\; E_f \;<\; E_i + k\,\frac{2\pi\hbar}{t_0}\,, \tag{4.3.36}$$

   with k some small integer, is narrow enough that $\rho(E)$ and $|V_{fi}|^2$ are approximately constant over this range. This allowed us to take them out of the integral simplifying greatly the problem and making a complete evaluation possible.

2. We cannot allow t_0 to be arbitrarily large. As we have

$$\sum_f P_{f\leftarrow i}(t_0) \;=\; w\,t_0\,, \tag{4.3.37}$$

   we must keep $wt_0 \ll 1$ for our first order calculation to be accurate.

Can the two conditions on t_0 be satisfied? There is no problem if the perturbation can be made small enough: indeed, suppose condition 1 is satisfied for some suitable t_0 but condition 2 is not. Then we can make the perturbation V smaller making w small enough that the second condition is satisfied. In practice, in specific problems, one could do the following check. First compute w assuming the golden rule. Then fix t_0 such that wt_0 is very small, say equal to 0.01. Then check that over the range $\sim \hbar/t_0$ the density of states and the matrix elements are roughly constant. If this works out the approximation should be very good!

Helium atom and autoionization. The helium has two protons ($Z = 2$) and two electrons. Let $H^{(0)}$ be the Hamiltonian for this system ignoring the the Coulomb repulsion between the electrons:

$$H^{(0)} \;=\; \frac{\mathbf{p}_1^2}{2m} - \frac{e^2}{r_1} \;+\; \frac{\mathbf{p}_2^2}{2m} - \frac{e^2}{r_2}\,. \tag{4.3.38}$$

Here the labels 1 and 2 refer to each one of the two electrons. The spectrum of this Hamiltonian consists of *hydrogenic states*, with n_1, n_2 the principal quantum numbers for the electrons. The energies are then

$$E_{n_1,n_2} = -(13.6\,\mathrm{eV})Z^2\left(\frac{1}{n_1^2}+\frac{1}{n_2^2}\right) = -(54.4\,\mathrm{eV})\left(\frac{1}{n_1^2}+\frac{1}{n_2^2}\right). \tag{4.3.39}$$

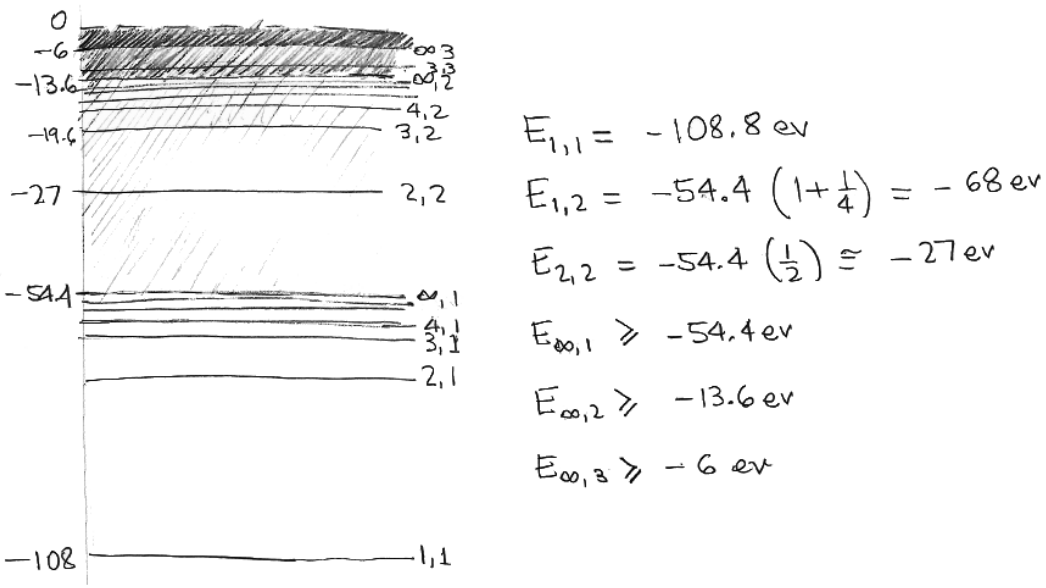


Figure 4.4: Hydrogenic states in helium and continuum states of negative total energy.

For the hydrogen atom we have bound states of negative energy and continuum states of positive energy that can be described to a good approximation as momentum eigenstates of the electron which is no longer bound to the proton. Since we have two electrons in the case of helium, there are continuum states in the spectrum with *negative* energy.

This first happens for $n_1 = 1$ in the limit as $n_2 \to \infty$. For $n_1 = 1$ and $n_2 = \infty$ the second electron is essentially free and contributes no energy. Thus a continuum appears for energy $E_{1,\infty} = -54.4$eV. This $(1S)(\infty)$ continuum extends for all $E \geq -54.4$eV as the free electron can have arbitrary positive kinetic energy. The state $(2S)(\infty)$ is the beginning of a second continuum, also including states of negative energy. In general the state $(nS)(\infty)$ with $n \geq 1$ marks the beginning of the n-th continuum. In each of these continua one electron is still bound and the other is free. A diagram showing some discrete states and a couple of continua is given in Figure 4.4.

Self-ionizing energy-conserving transitions can occur because discrete states can find themselves in the middle of a continuum. The state $(2S)^2$, for example, with two electrons on the $2S$ configuration and with energy $E_{2,2} = -27$eV is in the middle of the $(1S)(\infty)$ continuum. We can view the original $(2S)^2$ hydrogenic state as a $t = 0$ eigenstate of $H^{(0)}$ and treat the Coulomb repulsion as a perturbation. We thus have a total Hamiltonian H

that takes the form

$$H \;=\; H^{(0)} + V\,, \quad V = \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}\,. \tag{4.3.40}$$

The perturbation V produces "auto-ionizing" *Auger transitions* to the continuum. We have a transition from a state with energy $E_{2,2} = -27\text{eV}$ to a state of one bound electron with energy -54.4eV and one free electron with kinetic energy of 27eV. That final state is part of a continuum. Radiative transitions from $(2S)^2$ to $1S2S$, with photo-emission, are in fact a lot less likely than auto-ionizing transitions!

We will not do the quantitative analysis required to determine lifetime of the $(2S)^2$ state. In general auto-ionization is a process in which an atom or a molecule in an excited state spontaneously emits one of the outer-shell electrons. Auto-ionizing states are in general short lived. *Auger transitions* are auto-ionization processes in which the filling of an inner shell vacancy is accompanied by the emission of an electron. Our example of the $(2S)^2$ state is an Auger transition. Molecules can have auto ionizing Rydberg states, in which the little energy needed to remove the Rydberg electron is supplied by a vibrational excitation of the molecule.

4.3.2 Harmonic Perturbation

It is now time to consider the case when the perturbation is harmonic. We will be able to derive a similar looking Fermi golden rule for the transition rate. The most important difference is that now the transitions are of two types. They involve either absorption of energy or a release of energy. In both cases that energy (absorbed or released) is equal to $\hbar\omega$ where ω is the frequency of the perturbation.

As indicated in (4.3.3) we have

$$H(t) \;=\; H^{(0)} + \delta H(t)\,, \tag{4.3.41}$$

where the perturbation $\delta H(t)$ takes the form

$$\delta H(t) \;=\; \begin{cases} 0\,, & \text{for } \; t \le 0\,, \\ 2H'\cos\omega t\,, & \text{for } \; t > 0\,. \end{cases} \tag{4.3.42}$$

Here $\omega > 0$ and H' is some time independent Hamiltonian. The inclusion of an extra factor of two in the relation between δH and H' is convenient because it results in a golden rule does not have additional factors of two compared to the case of constant transitions.

We again consider transitions from an initial state i to a final state f. The transition amplitude this time From (4.2.33)

$$c_f^{(1)}(t_)) = \frac{1}{i\hbar}\int_0^{t_0} dt'\, e^{i\omega_{fi}t'}\,\delta H_{fi}(t')\,. \tag{4.3.43}$$

Using the explicit form of δH the integral can be done explicitly

$$\begin{aligned} c_f^{(1)}(t_0) &= \frac{1}{i\hbar}\int_0^{t_0} e^{i\omega_{fi}t'} 2H'_{fi}\cos\omega t' dt' \\ &= \frac{H'_{fi}}{i\hbar}\int_0^{t_0}\left(e^{i(\omega_{fi}+\omega)t'} + e^{i(\omega_{fi}-\omega)t'}\right)dt' \\ &= -\frac{H'_{fi}}{\hbar}\left[\frac{e^{i(\omega_{fi}+\omega)t_0}-1}{\omega_{fi}+\omega} + \frac{e^{i(\omega_{fi}-\omega)t_0}-1}{\omega_{fi}-\omega}\right]. \end{aligned} \tag{4.3.44}$$

Comments:

- The amplitude takes the form of a factor multiplying the sum of two terms, each one a fraction. As $t_0 \to 0$ each fraction goes to it_0. For finite t_0, which is our case of interest, each numerator is a complex number of bounded absolute value that oscillates in time from zero up to two. In comparing the two terms the relevant one is the one with the smallest denominator.[1]

- The first term is relevant as $\omega_{fi} + \omega \approx 0$, that is, when there are states at energy $E_f = E_i - \hbar\omega$. This is "stimulated emission", the source has stimulated a transition in which energy $\hbar\omega$ is released.

- The second term relevant if $\omega_{fi} - \omega \approx 0$, that is, when there are states at energy $E_f = E_i + \hbar\omega$. Energy is transferred from the perturbation to the system, and we have a process of "absorption".

Both cases are of interest. Let us do the calculations for the case of absorption; the answer for the case of spontaneous emission will be completely analogous. We take i to be a discrete state, possibly bound, and f to be a state in the continuum at the higher energy $E_f \approx E_i + \hbar\omega$. Since $\omega_{fi} \simeq \omega$, the second term in the last line of (4.3.44) is much more important than the first. Keeping only the second term we have

$$c_f^{(1)}(t_0) = -\frac{H'_{fi}}{\hbar}\frac{e^{\frac{i}{2}(\omega_{fi}-\omega)t_0}}{\omega_{fi}-\omega} 2i\sin\left(\frac{\omega_{fi}-\omega}{2}t_0\right), \tag{4.3.45}$$

and the transition probability is

$$P_{f\leftarrow i}(t_0) = |c_f^{(1)}(t_0)|^2 = \frac{4|H'_{fi}|^2}{\hbar^2}\frac{\sin^2\left(\frac{\omega_{fi}-\omega}{2}t_0\right)}{(\omega_{fi}-\omega)^2} \tag{4.3.46}$$

The transition probability is exactly the same as that for constant perturbations (see (4.3.20)) with V replaced by H' and ω_{fi} replaced by $\omega_{fi} - \omega$. The analysis that follows is

[1] This is like comparing two waves that are being superposed. The one with larger amplitude is more relevant even though at some special times, as it crosses the value of zero, it is smaller than the other wave.

completely analogous to the previous one so we shall be brief. Summing over final states we have

$$\sum_k P_{k\leftarrow i}(t_0) = \int P_{f\leftarrow i}\,\rho(E_f)dE_f = \int \frac{4|H'_{fi}|^2}{\hbar^2}\frac{\sin^2\left(\frac{\omega_{fi}-\omega}{2}t_0\right)}{(\omega_{fi}-\omega)^2}\rho(E_f)dE_f\,. \tag{4.3.47}$$

This time the main contribution comes from the region

$$-\frac{2\pi}{t_0} \;<\; \omega_{fi}-\omega \;<\; \frac{2\pi}{t_0} \tag{4.3.48}$$

In terms of the final energy this is the band

$$E_i+\hbar\omega-\frac{2\pi\hbar}{t_0} \;<\; E_f \;<\; E_i+\hbar\omega+\frac{2\pi\hbar}{t_0} \tag{4.3.49}$$

For sufficiently large t_0 this is the narrow band of states illustrated in Figure 4.5. Assume

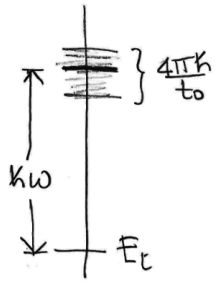


Figure 4.5: In the absorption process we must integrate over a narrow band of states about the final energy $E_i+\hbar\omega$.

that over the band H'_{fi} and the density of states is constant so that we get

$$\sum_k P_{k\leftarrow i}(t_0) = \frac{4}{\hbar}|H'_{fi}|^2\rho(E_i+\hbar\omega)\int \frac{\sin^2\left(\frac{\omega_{fi}-\omega}{2}t_0\right)}{(\omega_{fi}-\omega)^2}d\omega_{fi}\,. \tag{4.3.50}$$

Defining

$$u \equiv \tfrac{1}{2}\left(\omega_{fi}-\omega\right)t_0 \quad\rightarrow\quad du = \tfrac{1}{2}d\omega_{fi}\,t_0\,, \tag{4.3.51}$$

the integral in (4.3.50) becomes

$$\int_{-\infty}^{\infty}\frac{\sin^2 u}{\left(\frac{2u}{t_0}\right)^2}\frac{2}{t_0}du = \frac{t_0}{2}\int_{-\infty}^{\infty}\frac{\sin^2 u}{u^2}du \;=\; \frac{t_0}{2}\pi\,. \tag{4.3.52}$$

Finally, the transition probability is

$$\sum_k P_{k\leftarrow i}(t_0) \;=\; \frac{2\pi}{\hbar}|H'_{fi}|^2\rho(E_i+\hbar\omega)\,t_0\,. \tag{4.3.53}$$

The transition rate w is finally given by

$$\boxed{\text{Fermi's golden rule:}\quad w \;=\; \frac{2\pi}{\hbar}\rho(E_f)|H'_{fi}|^2\,,\quad E_f = E_i+\hbar\omega\,.} \tag{4.3.54}$$

Here $H'(t) = 2H'\cos\omega t$. Equation (4.3.54) is known as Fermi's golden rule for the case of harmonic perturbations. For the case of spontaneous emission the only change required in the above formula is $E_f = E_i - \hbar\omega$.

4.4 Ionization of hydrogen

We aim to find the ionization rate for hydrogen when hit by the harmonically varying electric field of an electromagnetic wave. We assume the hydrogen atom has its electron on the ground state. In this ionization process a photon ejects the bound electron, which becomes free.

Let us first do a few estimates to understand the validity of the approximations that will be required. If the electromagnetic field has frequency ω the incident photons have energy

$$E_\gamma = \hbar\omega\,. \tag{4.4.1}$$

The energy E_e and the magnitude k of the momentum of the ejected electron are given by

$$E_e = \frac{\hbar^2k^2}{2m} = E_\gamma - R_y\,, \tag{4.4.2}$$

where the Rydberg R_y is the magnitude of the energy of the ground state:

$$2R_y = \frac{e^2}{a_0} = \frac{\hbar^2}{ma_0^2} = \alpha\frac{\hbar c}{a_0}\,,\qquad R_y \simeq 13.6\text{ eV}\,. \tag{4.4.3}$$

Inequalities

1. Any electromagnetic wave has spatial dependence. We can ignore the spatial dependence of the wave if the wavelength λ of the photon is much bigger than the Bohr radius a_0:

$$\frac{\lambda}{a_0} \gg 1\,. \tag{4.4.4}$$

Such a condition puts an *upper* bound on the photon energy, since the more energetic photon the smaller its wavelength. To bound the energy we first write

$$\lambda = \frac{2\pi}{k_\gamma} = \frac{2\pi c}{\omega} = \frac{2\pi\hbar c}{\hbar\omega}\,, \tag{4.4.5}$$

and then find

$$\frac{\lambda}{a_0} = \frac{2\pi}{\hbar\omega}\frac{\hbar c}{a_0} = \frac{4\pi}{\alpha}\frac{R_y}{\hbar\omega} \simeq 1722\ \frac{R_y}{\hbar\omega} \tag{4.4.6}$$

The inequality (4.4.4) then gives

$$\hbar\omega \ll 1722\, R_y\ \simeq\ 23\,\text{keV} \tag{4.4.7}$$

2. For final states we would like to use free particle momentum eigenstates. This requires the ejected electron to be energetic enough not to be much effected by the Coulomb field. As a result, the photon to be energetic enough, and this constraint provides a *lower* bound for its energy. We have

$$E_e = E_\gamma - R_y \gg R_y \quad \rightarrow \quad \hbar\omega \gg R_y\,. \tag{4.4.8}$$

The two inequalities above imply

$$R_y \ll\ \hbar\omega\ \ll 1722\, R_y\,. \tag{4.4.9}$$

If consider that $1 \ll 10$ we could take

$$140\text{eV}\ \leq\ \hbar\omega\ \leq 2.3\,\text{keV}\,. \tag{4.4.10}$$

Note that even for the upper limit the electron is non relativistic: $2.3\,\text{keV} \ll m_e c^2 \simeq 511\text{keV}$.

Exercise: Determine ka_0 in terms of $\hbar\omega$ and R_y.
Solution:

$$\frac{\hbar^2 k^2}{2m} = \hbar\omega - R_y = R_y\left(\frac{\hbar\omega}{R_y} - 1\right) = \frac{\hbar^2}{2ma_0^2}\left(\frac{\hbar\omega}{R_y} - 1\right) \tag{4.4.11}$$

$$k^2 a_0^2 = \frac{\hbar\omega}{R_y} - 1 \quad \rightarrow \quad ka_0\ =\ \sqrt{\frac{\hbar\omega}{R_y} - 1}\,. \tag{4.4.12}$$

This is the desired result. In the range of (4.4.10) we have

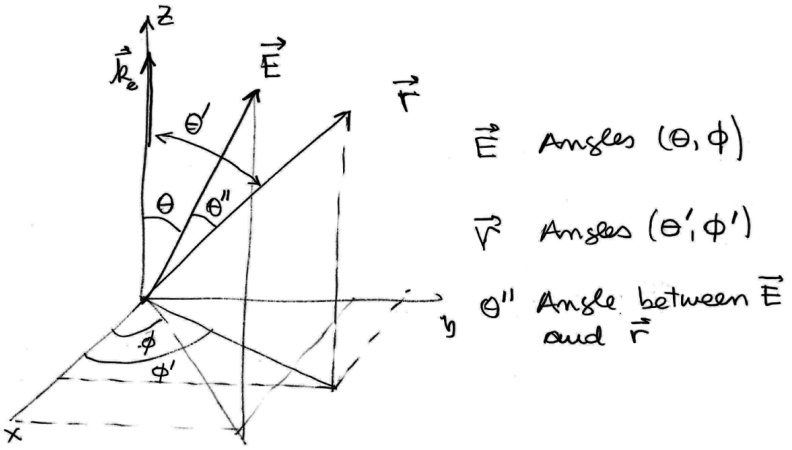
$$3\ \leq\ ka_0\ \leq\ 13\,. \tag{4.4.13}$$

Calculating the matrix element. Our perturbation Hamiltonian is

$$\delta H = -e\Phi\,, \tag{4.4.14}$$

where Φ is the electric scalar potential. Let the electric field at the atom be polarized in the $\hat{z}$ direction

$$\mathbf{E}(t) = E(t)\hat{z} = 2E_0 \cos\omega t\, \hat{z} \tag{4.4.15}$$



The associated scalar potential is

$$\Phi = -E(t)z\,, \tag{4.4.16}$$

and therefore

$$\delta H = eE(t)z = eE(t)r\cos\theta = 2\underbrace{eE_0 r\cos\theta}_{H'}\cos\omega t \equiv 2H'\cos\omega t \tag{4.4.17}$$

We have thus identified, in our notation,

$$H' \;=\; eE_0 r\cos\theta\,. \tag{4.4.18}$$

We want to compute the matrix element between an initial state $|i\rangle$ that is the ground state of hydrogen, and a final state $|f\rangle$ which is an electron plane wave with momentum $\mathbf{k}_e$. The associated wavefunctions are

$$\text{Final state:} \qquad u_{\mathbf{k}}(x) = \frac{1}{L^{3/2}}\,e^{i\mathbf{k}\cdot\mathbf{r}} \tag{4.4.19}$$

$$\text{Initial state:} \qquad \psi_0(r) = \frac{1}{\sqrt{\pi a_0^3}}\,e^{-\frac{r}{a_0}} \tag{4.4.20}$$

The only physical angle here is that between the ejected electron momentum $\mathbf{k}_e$ and the electric field polarization $\mathbf{E}$. We expect electron to be ejected maximally along $\mathbf{E}$. This suggests rearranging the axes to have the electron momentum along the z axis and and letting θ be the angle between the electron momentum and the electric field. The integration variable $\mathbf{r}$ will have angles θ', ϕ', and the angle between the electric field and $\mathbf{r}$ is now called θ'' as shown in the figure, so that $H' = eE_0 r\cos\theta''$:

$$\begin{aligned}\langle f|H'|i\rangle &= \int d^3x\,\frac{1}{L^{3/2}}\,e^{i\mathbf{k}\cdot\mathbf{r}}\,eE_0 r\cos\theta''\,\frac{1}{\sqrt{\pi a_0^3}}\,e^{-\frac{r}{a_0}} \\ &= \frac{eE_0}{\sqrt{\pi a_0^3 L^3}}\int r^2 dr\,\sin\theta' d\theta' d\phi' e^{ikr\cos\theta'} r\cos\theta'' e^{-\frac{r}{a_0}}\end{aligned} \tag{4.4.21}$$

The main complication with doing the integral is the factor $\cos\theta''$. The dot product of unit vectors along $\mathbf{E}$ and $\mathbf{n}$ is $\cos\theta''$:

$$\begin{aligned}\cos\theta'' &= (\sin\theta\cos\phi)(\sin\theta'\cos\phi') \;+\; (\sin\theta\sin\phi)(\sin\theta'\sin\phi') \;+\; \cos\theta\cos\theta' \\ &= \sin\theta\sin\theta'\cos(\phi-\phi') + \cos\theta\cos\theta' \end{aligned} \tag{4.4.22}$$

Since the following integral vanishes

$$\int d\phi' \cos(\phi-\phi') = 0 \tag{4.4.23}$$

the first term in the expression for $\cos\theta''$ will vanish upon ϕ' integration. We therefore can replace $\cos\theta'' \to \cos\theta\cos\theta'$ to find

$$\begin{aligned}\langle f|H'|i\rangle &= \frac{eE_0}{\sqrt{\pi a_0^3 L^3}} \int r^3 dr\, \sin\theta' d\theta' d\phi' e^{ikr\cos\theta'} \cos\theta\cos\theta' e^{-\frac{r}{a_0}} \\ &= \frac{eE_0}{\sqrt{\pi a_0^3 L^3}} (\cos\theta)(2\pi) \int r^3 dr\, e^{-\frac{r}{a_0}} \int_{-1}^{1} d(\cos\theta') \cos\theta' e^{ikr\cos\theta'} \end{aligned} \tag{4.4.24}$$

Now let $r = a_0 u$ and do the radial integration:

$$\begin{aligned}\langle f|H'|i\rangle &= \frac{eE_0}{\sqrt{\pi a_0^3 L^3}} 2\pi\cos\theta a_0^4 \int_{-1}^{1} d(\cos\theta')\cos\theta' \int u^3 du\, e^{-u(1+ika_0\cos\theta')} \\ &= \frac{eE_0}{\sqrt{\pi a_0^3 L^3}} 2\pi\cos\theta a_0^4 \int_{-1}^{1} d(\cos\theta')\cos\theta' \frac{3!}{(1+ika_0\cos\theta')^4}\,. \end{aligned} \tag{4.4.25}$$

Writing $x = \cos\theta'$ the angular integral is not complicated:

$$\begin{aligned}\langle f|H'|i\rangle &= \frac{eE_0}{\sqrt{\pi a_0^3 L^3}}\; 2\pi\cos\theta a_0^4 \frac{3!}{(ika_0)^4} \int_{-1}^{1} \frac{x}{\left(x+\frac{1}{ika_0}\right)^4} dx \\ &= \frac{eE_0}{\sqrt{\pi a_0^3 L^3}}\; 2\pi\cos\theta a_0^4 \frac{3!}{(ika_0)^4} \frac{8\left(\frac{1}{ika_0}\right)}{3\left(1+\frac{1}{k^2a_0^2}\right)^3} \\ &= -i\frac{32\pi eE_0 a_0}{\sqrt{\pi a_0^3 L^3}} \frac{ka_0^4}{(1+k^2a_0^2)^3}\cos\theta \end{aligned} \tag{4.4.26}$$

Hence, with a little rearrangement

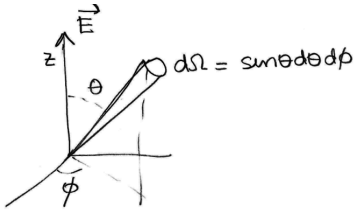
$$\boxed{\langle f|H'|i\rangle \;=\; -i32\sqrt{\pi}\,(eE_0a_0)\,\frac{ka_0^4}{\sqrt{a_0^3L^3}}\;\frac{1}{(1+k^2a_0^2)^3}\;\cos\theta\,.} \tag{4.4.27}$$

The above matrix element has the units of (eE_0a), which is energy. This is as expected. Squaring we find

$$|H'_{fi}|^2 \;=\; 1024\,\pi\,(eE_0a)^2\,\frac{k^2a_0^5}{L^3}\;\frac{\cos^2\theta}{(1+k^2a_0^2)^6} \tag{4.4.28}$$

At this point, with θ the angle between $\mathbf{k}_e$ and $\mathbf{E}$, it is more convenient to align $\mathbf{E}$ along the z-axis and let $\mathbf{k}_e$ be defined by the polar angles θ, ϕ. The density of states was given in (4.3.14)

$$\rho(E_e) = \frac{L^3}{8\pi^3}\frac{m}{\hbar^2}k\,d\Omega \tag{4.4.29}$$



so that using Fermi's Golden rule, the rate dw to go into final states in the solid angle $d\Omega$ is

$$\begin{aligned} dw &= \frac{2\pi}{\hbar}\rho(E_e)|H'_{fi}|^2 \\ &= \frac{2\pi}{\hbar}\,\frac{L^3}{8\pi^3}\frac{m}{\hbar^2}k\,d\Omega\;1024\pi(eE_0a_0)^2\frac{k^2a_0^5}{L^3}\frac{\cos^2\theta}{(1+k^2a_0^2)^6}\,. \end{aligned} \tag{4.4.30}$$

It follows that

$$\boxed{\frac{dw}{d\Omega} = \frac{256}{\pi}\,\frac{ma_0^2}{\hbar^2}\,\frac{(eE_0a_0)^2}{\hbar}\,\frac{k^3a_0^3}{(1+k^2a_0^2)^6}\,\cos^2\theta\,.} \tag{4.4.31}$$

$\frac{dw}{d\Omega}$ is the probability of ionization per unit time and per unit solid angle. All the ejected electrons will have the same momentum $\hbar k$. Note that the units have worked out: $w \sim \frac{[E]^2}{\hbar}\cdot\frac{1}{[E]} \sim \frac{1}{T}$ as expected. In here $2E_0$ is the peak amplitude of the electric field in the wave. The $\cos^2\theta$ implies that the electron tends to be ejected in the direction of the electric field.

The total ionization probability per unit time is obtained by integration over solid angle. Using

$$\int \cos^2\theta\,d\Omega = \tfrac{1}{3}\,4\pi\,, \tag{4.4.32}$$

and recalling that $\frac{\hbar^2}{ma_0^2} = 2R_y$

$$w = \int d\Omega\frac{dw}{d\Omega} = \frac{512}{3}\,\frac{(eE_0a_0)^2}{\hbar R_y}\,\frac{k^3a_0^3}{(1+k^2a_0^2)^6}\,. \tag{4.4.33}$$

For the window of validity (4.4.13) we have $9 \le (ka_0)^2 \le 169$, and we neglect the "one" in the denominator to get

$$w = \frac{512}{3}\,\frac{(eE_0a_0)^2}{\hbar R_y}\,\frac{1}{(ka_0)^9}\,. \tag{4.4.34}$$

This is our final answer. For numerical calculations it is useful to note the atomic units in which the answer takes the form

$$w = \frac{256}{3}\left(\frac{E_p}{E_*}\right)^2\frac{1}{t_*}\,\frac{1}{(ka_0)^9}\,. \tag{4.4.35}$$

Here $E_p = 2E_0$ is the peak amplitude of the electric field. Moreover, the atomic electric field E_* and the atomic time t_* are given by

$$\begin{aligned} E_* &= \frac{2R_y}{ea_0} = \frac{e}{a_0^2} = 5.14 \times 10^{11}\text{V/m} \\ t_* &= \frac{a_0}{\alpha c} = 2.42 \times 10^{-17}\text{ sec.} \end{aligned} \tag{4.4.36}$$

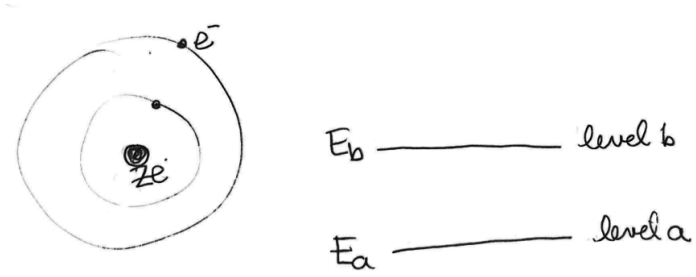
Note that E_* is the electric field of a proton at a distance a_0 while t_* is the time it takes the electron to travel a distance a_0 at the velocity αc in the ground state. A laser intensity of $3.55 \times 10^{16}\text{W/cm}^2$ has an peak electric field of magnitude E_*.

4.5 Light and atoms

4.5.1 Absorption and stimulated emission

The physical problem we are trying to solve consists of a collection of atoms with two possible energy levels interacting with light at a temperature T. We want to understand the processes of absorption and emission of radiation and how they can produce thermal equilibrium.

Let us first consider a single atom and the possible processes. Consider two possible levels of an electron in an atom



Define

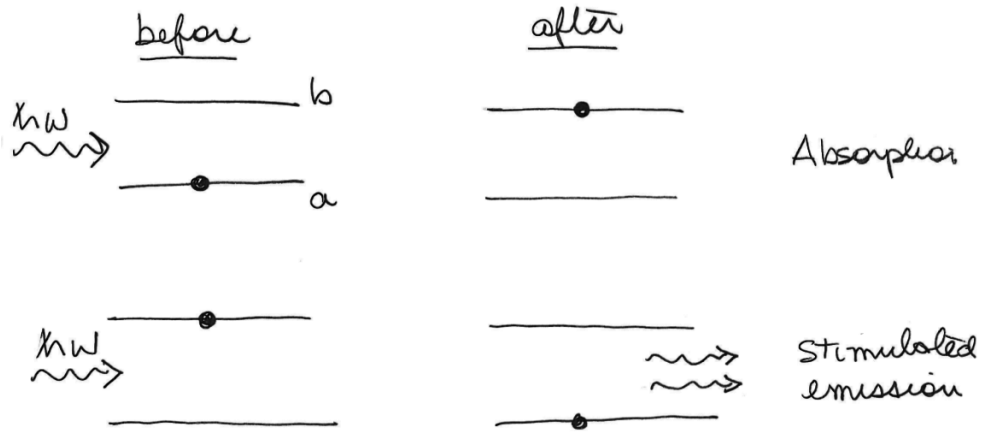
$$\omega_{ab} \equiv \frac{E_b - E_a}{\hbar}\,.$$

Imagine now shining light into the atom at a frequency ω_{ab}. There are two possibilities depending on the initial state of the atom:

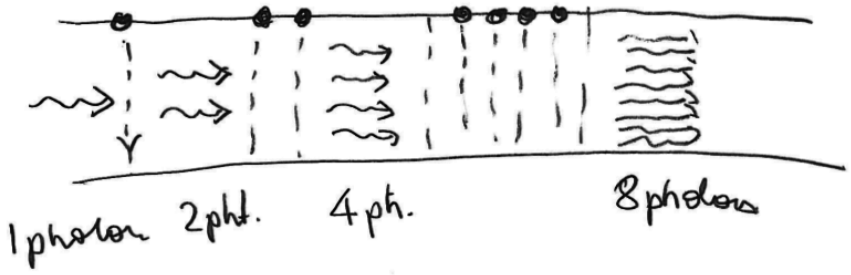
(i) Electron initially in $|a\rangle$: there will be an *absorption rate* at which a photon is absorbed and the electron goes from $|a\rangle \to |b\rangle$.

(ii) Electron initially in $|b\rangle$: there will be a *stimulated emission rate* at which the photon field stimulates an electronic transition $|b\rangle \to |a\rangle$ with the release of an additional photon.

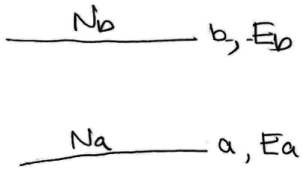
These processes are illustrated in the figure below:



A LASER, *Light Amplification by Stimulated Emission of Radiation*, works by having population inversion, namely most of the atoms are in the excited energy level. Then any small number of photons can trigger larger and larger numbers of stimulated emission processes!



4.5.2 Einstein's Argument



Atoms in states a or b with $E_b > E_a$, with populations N_a and N_b respectively. The atoms are in equilibrium with a bath of photons all at temperature T. Einstein discovered a number of relations from the condition of equilibrium.

Fact 1: Equilibrium values for populations:

$$\dot{N}_a = \dot{N}_b = 0 \tag{4.5.1}$$

Fact 2: Equilibrium populations governed by thermal distribution

$$\frac{N_a}{N_b} = \frac{e^{-\beta E_b}}{e^{-\beta E_a}} = e^{-\beta\hbar\omega_{ab}}\,, \quad \beta \equiv \frac{1}{k_b T} \tag{4.5.2}$$

Fact 3: For a thermal blackbody, the energy $U(\omega)d\omega$ per unit volume in the frequency range $d\omega$ is known to be

$$U(\omega)d\omega = \frac{\hbar}{\pi^2 c^3}\frac{\omega^3 d\omega}{e^{\beta\hbar\omega}-1} \tag{4.5.3}$$

Process		Rate
Absorption:	$\|a\rangle \to \|b\rangle$ photon absorbed	$B_{ab}U(\omega_{ba})N_a$
Stimulated emission:	$\|b\rangle \to \|a\rangle$ photon released	$B_{ba}U(\omega_{ba})N_b$

In the table above we have indicated the two obvious processes: absorption and stimulated emission. The rate indicated is the number of transitions per unit time. For absorption, this rate is proportional to the number N_a of atoms in the ground state, capable of absorbing a photon, times $U(\omega_{ab})$ which captures the information about the number of photons available, times a B coefficient B_{ab} that we want to determine. For stimulated emission, the rate is proportional to the number N_b of atoms in the excited state, thus capable of emitting a photon, times $U(\omega_{ab})$ times a B coefficient B_{ba}. The inclusion of $U(\omega_{ab})$ reflects the "stimulated" character of the transition.

Can we make this work, that is, can we achieve equilibrium? We will see that we *cannot*. With the two processes above, the rate of change of N_b is

$$\dot{N}_b \;=\; \text{rate absorption} - \text{rate stimulated emission} \tag{4.5.4}$$

At equilibrium $\dot{N}_b = 0$, hence

$$\begin{aligned} 0 = \dot{N}_b &= B_{ab}U(\omega_{ba})N_a - B_{ba}U(\omega_{ba})N_b \\ &= (B_{ab}N_a - B_{ba}N_b)U(\omega_{ba}) \\ 0 &= N_a\left(B_{ab} - B_{ba}e^{-\beta\hbar\omega_{ba}}\right)U(\omega_{ba}) \end{aligned} \tag{4.5.5}$$

This is a strange result: in order to have equilibrium we need $B_{ab} - B_{ba}e^{-\beta\hbar\omega_{ba}} = 0$. The B coefficients, however, depend on the electronic configurations in the atom and *not* on the temperature T. Thus this cancellation is not possible for arbitrary temperature. We also note that the photon energy density does not feature in the equilibrium condition. In conclusion, equilibrium is not possible.

What are we missing? Another process: *spontaneous emission!!*, an emission rate that does not depend on the thermal photons. The rate is proportional to the number of atoms N_b in the excited state, with a coefficient of proportionality called A:

Process		Rate
Spontaneous emission:	$\|b\rangle \to \|a\rangle$ photon released	AN_b

Reconsider now the equilibrium condition with this extra contribution to $\dot{N}_b$:

$$\begin{aligned} 0 = \dot{N}_b &= B_{ab}U(\omega_{ba})N_a - B_{ba}U(\omega_{ba})N_b - AN_b \\ \implies A &= \left(B_{ab}\frac{N_a}{N_b} - B_{ba}\right)U(\omega_{ba}) \\ \implies U(\omega_{ba}) &= \frac{A}{B_{ab}}\,\frac{1}{e^{\beta\hbar\omega_{ba}} - \frac{B_{ba}}{B_{ab}}} \end{aligned} \tag{4.5.6}$$

The equilibrium condition indeed gives some important constraint on $U(\omega_{ab})$. But from Eq. (4.5.3) we know

$$U(\omega_{ba}) = \frac{\hbar\,\omega_{ba}^3}{\pi^2 c^3}\,\frac{1}{e^{\beta\hbar\omega_{ba}} - 1} \tag{4.5.7}$$

Hence comparing the two equations we get

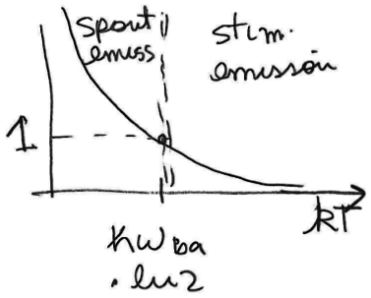
$$B_{ab} = B_{ba} \qquad \text{and} \qquad \frac{A}{B_{ab}} = \frac{\hbar\omega_{ba}^3}{\pi^2 c^3} \tag{4.5.8}$$

As we'll see, we'll be able to calculate B_{ab}, but A is harder. Happily, thanks to (4.5.8), we can obtain A from B_{ab}.

Spontaneous emission does not care about $U(\omega_{ba})$; the photons flying around. At a deep level one can think of spontaneous emission as stimulated emission due to vacuum fluctuation of the EM field.

For a given atomic transition expect stimulated emission rate to dominate at higher temperature, the there are more photons around. Spontaneous emission should dominate at very low temperature. Indeed from (4.5.6)

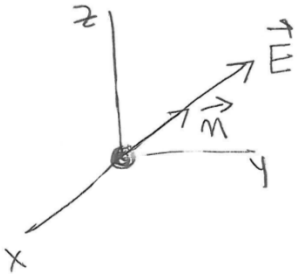
$$\frac{A}{B_{ab}U(\omega_{ba})} = \exp\left(\frac{\hbar\,\omega_{ba}}{k_b T}\right) - 1$$



4.5.3 Atom/light interaction

Focus on $\vec{E}$ field. Effects of $\vec{B}$ are weaker by $\mathcal{O}\left(\frac{v}{c}\right) \sim \alpha$. For optical frequencies $\lambda \sim 4000 - 8000\,\text{Å}$ and since $a_0 \simeq 0.5\,\text{Å}$, we can ignore the spatial dependence of the field (even for ionization frequencies $\frac{\lambda}{a_0} \sim 1700$)
Electric field at the atom

$$\mathbf{E}(t) = E(t)\mathbf{n} = 2E_0 \cos(\omega t)\mathbf{n}$$



where $\mathbf{n}$ is the direction of the field.

$$\Phi(\mathbf{r}, t) = -\mathbf{r} \cdot \mathbf{E}(t)\,, \quad \nabla\Phi = -\mathbf{E} \tag{4.5.9}$$

as expected. The perturbation is therefore

$$\delta H = +q\Phi(\mathbf{r}) = -q\mathbf{r} \cdot \mathbf{E}(t) \tag{4.5.10}$$

By defining the dipole moment $\boldsymbol{d}$ as $\boldsymbol{d} \equiv q\mathbf{r}$, we can rewrite the perturbation as

$$\delta H = -\boldsymbol{d} \cdot \mathbf{E}(t) = -\boldsymbol{d} \cdot \mathbf{n} 2E_0 \cos(\omega t) = 2(-\boldsymbol{d} \cdot \mathbf{n} E_0) \cos(\omega t)\,. \tag{4.5.11}$$

Since we defined $\delta H = 2H' \cos \omega t$ we can read

$$H' = -\boldsymbol{d} \cdot \mathbf{n}\, E_0\,. \tag{4.5.12}$$

Recall that to first order in perturbation theory $P_{b\leftarrow a}(t) = P_{a\leftarrow b}(t)$ so let's consider just $P_{a\leftarrow b}(t)$, the stimulated emission process, from (4.3.46)

$$P_{a\leftarrow b}(t) = \frac{4|H'_{ab}|^2}{\hbar^2} \frac{\sin^2\left(\frac{\omega_{ba}-\omega}{2}t\right)}{(\omega_{ba}-\omega)^2} = \frac{4E_0^2|(\boldsymbol{d}\cdot\mathbf{n})_{ab}|^2}{\hbar^2} \frac{\sin^2\left(\frac{\omega_{ba}-\omega}{2}t\right)}{(\omega_{ba}-\omega)^2} \tag{4.5.13}$$

Now think in terms of energy. The energy density u_E in the electric field $E(t) = 2E_0 \cos(\omega t)\mathbf{n}$ is

$$u_E = \frac{|E(t)|^2}{8\pi} = \frac{4E_0^2}{8\pi} \cos^2 \omega t \implies \langle u_E \rangle_{\text{time}} = \frac{4E_0^2}{8\pi} \cdot \frac{1}{2} = \frac{E_0^2}{4\pi}\,. \tag{4.5.14}$$

In a wave the electric and magnetic energy are the same and therefore

$$\langle u \rangle_{\text{time}} = 2\langle u_E \rangle_{\text{time}} = \frac{E_0^2}{2\pi} \implies E_0^2 = 2\pi\langle u \rangle \tag{4.5.15}$$

The superposition of light is incoherent, so we will add probabilities of transition due to each component of light. For this we must turn a sum of electric field intensities into an integral.

$$\sum_i E_0^2(\omega_i) = 2\pi \int U(\omega) d\omega \tag{4.5.16}$$

where $U(\omega)$ is the energy density per unit frequency. In this way the transition rate in terms of energy reads

$$\begin{aligned} P_{a\leftarrow b}(t) &= \frac{|(\boldsymbol{d}\cdot\mathbf{n})_{ab}|^2}{\hbar^2} 2\pi \int U(\omega) d\omega \, \frac{\sin^2\left(\frac{\omega_{ba}-\omega}{2}t\right)}{(\omega_{ba}-\omega)^2} \\ &= \frac{|(\boldsymbol{d}\cdot\mathbf{n})_{ab}|^2}{\hbar^2} (2\pi) U(\omega_{ab}) \int d\omega \, \frac{\sin^2\left(\frac{\omega_{ba}-\omega}{2}t\right)}{(\omega_{ba}-\omega)^2} \end{aligned} \tag{4.5.17}$$

As usual, take $x \equiv \left(\frac{\omega_{ba}-\omega}{2}t\right) \implies d\omega = 2\frac{dx}{t}$, so that (4.5.17) is

$$\frac{2}{t}\cdot t^2 \int \frac{\sin^2 x}{x^2} dx = 2t\pi \tag{4.5.18}$$

$$\boxed{R_{a\leftarrow b} = \frac{4\pi^2}{\hbar^2} |(\boldsymbol{d}\cdot\mathbf{n})_{ab}|^2 U(\omega_{ba})} \tag{4.5.19}$$

So far we have two vectors: $\boldsymbol{d}$ which depends on the atom geometry and $\mathbf{n}$ which is the direction of the electric field. Since light comes in all possible polarization, this amounts to averaging over all possible directions of $\mathbf{n}$

$$\left\langle |\boldsymbol{d}_{ab}\cdot\mathbf{n}|^2 \right\rangle = \left\langle \left| \sum_i d_{ab}^i n_i \right|^2 \right\rangle = \left\langle \left(\sum_i d_{ab}^i n_i \right)^* \left(\sum_j d_{ab}^j n_j \right) \right\rangle = \sum_{i,j} (d_{ab}^i)^* (d_{ab}^j) \langle n_i n_j \rangle \tag{4.5.20}$$

Expect

$$\langle n_x n_x \rangle = \langle n_y n_y \rangle = \langle n_z n_z \rangle \tag{4.5.21}$$

Since

$$\left\langle \sum_i n_i n_i \right\rangle = \langle n^2 \rangle = 1 \tag{4.5.22}$$

then

$$\langle n_i n_j \rangle = \frac{1}{3}\delta_{ij} \tag{4.5.23}$$

$$\left\langle |\boldsymbol{d}_{ab}\cdot\mathbf{n}|^2 \right\rangle = \frac{1}{3}\boldsymbol{d}_{ab}^*\cdot\boldsymbol{d}_{ab} \equiv \frac{1}{3}|\boldsymbol{d}_{ab}|^2 \tag{4.5.24}$$

This is the magnitude of a complex vector!

$$\boxed{R_{a\leftarrow b} = \frac{4\pi^2}{3\hbar^2}|\boldsymbol{d}_{ab}|^2 U(\omega_{ba})} \tag{4.5.25}$$

This is the transition probability per unit time for a single atom

$$B_{ab} = \frac{4\pi^2}{3\hbar^2}|\boldsymbol{d}_{ab}|^2 \tag{4.5.26}$$

thus recalling (4.5.8)

$$A = \frac{\hbar\omega_{ba}^3}{\pi^2c^3}B_{ab} = \frac{\hbar\omega_{ba}^3}{\pi^2c^3}\frac{4\pi^2}{3\hbar^2}|\boldsymbol{d}_{ab}|^2 \tag{4.5.27}$$

hence we have that A, the transition probability per unit time for an atom to go from $|b\rangle \to |a\rangle$, is

$$\boxed{A \;=\; \frac{4}{3}\,\frac{\omega_{ba}^3}{\hbar c^3}\;|\boldsymbol{d}_{ab}|^2\,.} \tag{4.5.28}$$

The lifetime for the state is $\tau = \frac{1}{A}$. The number N of particles decays exponentially in time

$$\frac{dN}{dt} = -AN \implies N(t) = e^{-At} = N_0 e^{-t/\tau} \tag{4.5.29}$$

If there are various decay possibilities $A_1, A_2, \ldots$, the transition rates add

$$A_{\text{tot.}} = A_1 + A_2 + \ldots \qquad \text{and} \qquad \tau = \frac{1}{A_{\text{tot.}}} \tag{4.5.30}$$

4.5.4 Selection rules

(to be covered in recitation) Given two states $|n\ell m\rangle$ and $|n'\ell'm'\rangle$, when $\langle n\ell m|\mathbf{r}|n'\ell'm'\rangle \neq 0$? One can learn that

$$\langle n\ell m|z|n'\ell'm'\rangle = 0 \qquad \text{for } m' \neq m \tag{4.5.31}$$

$$\langle n\ell m|x|n'\ell'm'\rangle = \langle n\ell m|y|n'\ell'm'\rangle = 0 \qquad \text{for } m' \neq m \pm 1 \tag{4.5.32}$$

Hence no transition unless

$$\Delta m \equiv m' - m = 0, \pm 1 \tag{4.5.33}$$

Additionally

$$\Delta\ell \equiv \ell' - \ell = \pm 1 \tag{4.5.34}$$

Chapter 6: Adiabatic approximation

B. Zwiebach
June 2, 2017

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1 Introduction

1.1 Adiabatic approximation in Classical Mechanics

Let's go back to classical mechanics, with a harmonic oscillator performing motion but with $\omega(t)$ not constant. The hamiltonian of the system would be

$$H(x,p,\omega(t)) = \frac{p^2}{2m} + \frac{1}{2}m\omega^2(t)x^2 \tag{1.1}$$

where x and p are going to be functions of time.
In general

$$\frac{dH}{dt} = \frac{\partial H}{\partial x}\dot{x} + \frac{\partial H}{\partial p}\dot{p} + \frac{\partial H}{\partial t}\,. \tag{1.2}$$

Hamilton's equation of motion read

$$\frac{\partial H}{\partial p} = \dot{x}\,, \qquad \frac{\partial H}{\partial x} = -\dot{p}\,. \tag{1.3}$$

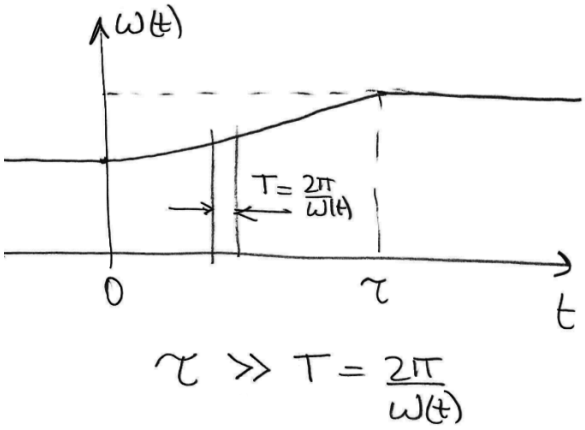
Even if you are not familiar with these, you probably know well their quantum analogs:

$$\begin{aligned} i\hbar\frac{d\langle x\rangle}{dt} &= \langle[x,H]\rangle = \left\langle i\hbar\frac{\partial H}{\partial p}\right\rangle \quad \rightarrow \quad \frac{d\langle x\rangle}{dt} = \left\langle\frac{\partial H}{\partial p}\right\rangle \\ i\hbar\frac{d\langle p\rangle}{dt} &= \langle[p,H]\rangle = \left\langle -i\hbar\frac{\partial H}{\partial x}\right\rangle \quad \rightarrow \quad \frac{d\langle p\rangle}{dt} = -\left\langle\frac{\partial H}{\partial x}\right\rangle \end{aligned} \tag{1.4}$$

At any rate, equations (1.3) imply that the first two terms in the right-hand side of (1.2) vanish and we have

$$\frac{dH}{dt} = \frac{\partial H}{\partial t} = m\omega\dot{\omega}x^2\,. \tag{1.5}$$

We have an *adiabatic* change if the time scale τ for change is much greater than time scale of the oscillation, $T = \frac{2\pi}{\omega(t)}$.



What remains roughly constant as $\omega(t)$ changes adiabatically?

$$\textbf{Claim:} \qquad I(t) \equiv \frac{H(t)}{\omega(t)} \qquad \text{is almost constant in adiabatic changes of } \omega. \tag{1.6}$$

$I(t)$ is called *the adiabatic invariant.*
Let us see why this is so:

$$\begin{aligned} \frac{dI}{dt} &= \frac{1}{\omega^2}\left(\omega\frac{dH}{dt} - H(t)\dot{\omega}\right) = \frac{1}{\omega^2}\left(\omega\left(m\omega\dot{\omega}x^2\right) - \left(\frac{p^2}{2m} + \tfrac{1}{2}m\omega^2(t)x^2\right)\dot{\omega}\right) = \\ &= \frac{\dot{\omega}}{\omega^2}\left(\tfrac{1}{2}m\omega^2(t)x^2 - \frac{p^2}{2m}\right) = \frac{\dot{\omega}}{\omega^2}\left(V(t) - K(t)\right)\,, \end{aligned} \tag{1.7}$$

where V and K are the potential and kinetic energies, respectively. We want to understand why this right-hand side is small. Clearly, $\frac{\dot{\omega}}{\omega^2}$ is slowly varying if $\dot{\omega}$ is slowly varying, but the term in parenthesis is actually quickly varying. Indeed, with

$$x = A\sin\omega t \quad \text{and} \quad p = Am\omega\cos\omega t$$

then the parenthesis goes like

$$\left(\tfrac{1}{2}m\omega^2x^2 - \frac{p^2}{2m}\right) \sim \tfrac{1}{2}m\omega^2(\sin^2\omega t - \cos^2\omega t) \sim -\tfrac{1}{2}m\omega^2\cos 2\omega t\,, \tag{1.8}$$

which is a fast variation. Let us see, however, how much $I(t)$ changes over one period

$$I(t+T) - I(t) = \int_t^{t+T} \frac{dI}{dt'} dt' = \int_t^{t+T} \frac{\dot{\omega}}{\omega^2}(t') \left(V(t') - K(t')\right) dt' \tag{1.9}$$

Since $\omega(t)$ is slowly varying, it changes very little over a period T and we can take the factor $\dot{\omega}/\omega$ out of the integral:

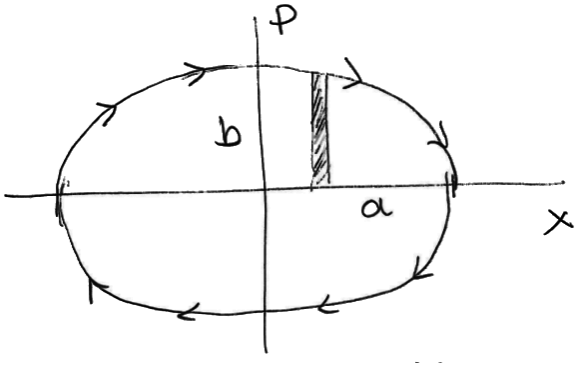
$$I(t+T) - I(t) \simeq \frac{\dot{\omega}}{\omega^2}(t) \int_t^{t+T} \left(V(t) - K(t)\right) dt' \tag{1.10}$$

In harmonic motion with ω constant, the *average* over a period of the potential energy $V(t)$ is exactly equal to the average of the kinetic energy $K(t)$, and the two terms above would cancel exactly. When ω is slowly changing they roughly cancel

$$I(t+T) - I(t) \simeq \frac{\dot{\omega}(t)}{\omega^2} \cdot 0 \simeq 0 \tag{1.11}$$

What is the geometrical interpretation of the adiabatic invariant E/ω? For this we consider the motion of a classical oscillator in phase space (x, p) where periodic oscillations trace the ellipse defined by energy conservation:

$$\frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2 = E \qquad (\omega, E, \text{constants})$$



We quickly see that the semi-major and semi-minor axes have lengths

$$a = \sqrt{\frac{2E}{m\omega^2}} \quad \text{and} \quad b = \sqrt{2mE} \tag{1.12}$$

Therefore

$$\text{Area of the ellipse } = \pi ab = 2\pi \frac{E}{\omega} \tag{1.13}$$

The adiabatic invariant is proportional to the area of the ellipse. That's neat! We can rewrite the area as an integral that takes a familiar form:

$$\text{Area of the ellipse } = \oint p\, dx$$

where we integrate over the *whole* closed trajectory with the orientation shown in the picture so that the area above the x axis is obtained as we go from left to right and the area under the x axis is obtained as we go from right to left. In this example

$$\oint p\,dx = 2\pi I\,. \tag{1.14}$$

More generally, for other systems the left-hand side is an adiabatic invariant. The value of the invariant is different for different systems, for the oscillator it is $2\pi E/\omega$.

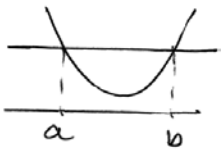
1.2 Quantum mechanics systems

What does it suggest for quantum mechanics?
First, for the harmonic oscillator

$$\frac{E}{\omega} = \frac{\hbar\omega\left(n+\frac{1}{2}\right)}{\omega} = \hbar\left(n+\tfrac{1}{2}\right) \tag{1.15}$$

Fixed $\frac{E}{\omega}$ is fixed quantum number! This suggests that in QM the quantum number doesn't tend to change under adiabatic changes. Indeed, we get the same intuition from WKB: consider a potential with two turning points a, b. We have the Bohr-Sommerfield quantization condition

$$\frac{1}{\hbar}\int_a^b p(x)dx = \left(n+\tfrac{1}{2}\right)\pi$$



rewritten as

$$\oint p(x)dx = 2\pi\hbar\left(n+\tfrac{1}{2}\right) \tag{1.16}$$

The left hand side, as noted before is an adiabatic invariant, so in the semiclassical approximation for *arbitrary* potential we find that the quantum number may not change under adiabatic changes! We will see that indeed that is the case.

The formula for transitions at first order in perturbation theory gives complementary intuition:

$$P_{f\leftarrow i}(t) = \left|\int_0^t e^{i\omega_{fi}t}\,\frac{\widetilde{\delta H}_{fi}(t')}{i\hbar}\,dt'\right|^2 \tag{1.17}$$

For constant perturbations, $\widetilde{\delta H}_{fi}$ is time-independent and

$$P_{f\leftarrow i}(t) = \frac{|\widetilde{\delta H}_{fi}|^2}{\hbar^2}\left|\int_0^t e^{i\omega_{fi}t}\,dt'\right|^2 = \frac{|\widetilde{\delta H}_{fi}|^2}{\hbar^2}\frac{\left|e^{i\omega_{fi}T}-1\right|^2}{\omega_{fi}^2}\,. \tag{1.18}$$

- If the spectrum is discrete, it is hard to jump a big energy gap because of the $\frac{1}{\omega_{fi}^2}$ suppression.
- For slowly varying perturbations (compared to ω_{fi}) the $\frac{1}{\omega_{fi}^2}$ suppression will remain.

So it is difficult in general to change state with constant or slow perturbations, suggesting again that quantum numbers are adiabatic invariants. That is why transitions to the continuum with constant perturbations essentially conserve energy. And why you need oscillatory perturbations for efficient transitions between energy levels.

2 Adiabatic Evolution

Suppose you have found a $\psi(t)$ such that

$$H(t)|\psi(t)\rangle = E(t)|\psi(t)\rangle \tag{2.1}$$

we'll call $|\psi(t)\rangle$, defined by (2.1), an **instantaneous eigenstate**. I'd like to emphasize from the start that, in general, an instantaneous eigenstate *is not a solution* of the time dependent Schrödinger equation. As it turns out, it is a useful tool to construct approximate solutions to the Schrödinger equation.

Let us try to understand the relation between $|\psi(t)\rangle$ and $|\Psi(t)\rangle$, the solution to the Schrödinger equation

$$i\hbar\partial_t|\Psi(t)\rangle = H(t)|\Psi(t)\rangle\,. \tag{2.2}$$

Let us try an ansatz, building the solution $|\Psi(t)\rangle$ using the instantaneous eigenstate:

$$|\Psi(t)\rangle = c(t)\exp\left(\frac{1}{i\hbar}\int_0^t E(t')dt'\right)|\psi(t)\rangle\,, \tag{2.3}$$

with $c(t)$ a function of time to be determined and where we have included a familiar time dependent phase. There is *no guarantee* this ansatz will work but it seems a good try.

The LHS of the Schrödinger equation then looks like

$$i\hbar\partial_t|\Psi(t)\rangle = \dot{c}\,(t)\exp\left(\frac{1}{i\hbar}\int_0^t E(t')dt'\right)|\psi(t)\rangle + E(t)|\Psi(t)\rangle + c(t)\exp\left(\frac{1}{i\hbar}\int_0^t E(t')dt'\right)|\dot{\psi}(t)\rangle \tag{2.4}$$

For the RHS, using the instantaneous eigenstate equation, we have

$$H(t)|\Psi(t)\rangle = c(t)\exp\left(\frac{1}{i\hbar}\int_0^t E(t')dt'\right)H(t)|\psi(t)\rangle \;=\; E(t)|\Psi(t)\rangle\,. \tag{2.5}$$

Equating the two sides, we get

$$\dot{c}(t)\exp\left(\frac{1}{i\hbar}\int_0^t E(t')dt'\right)|\psi(t)\rangle + c(t)\exp\left(\frac{1}{i\hbar}\int_0^t E(t')dt'\right)|\dot{\psi}(t)\rangle = 0$$

and canceling the two exponentials we have

$$\boxed{\dot{c}(t)\,|\psi(t)\rangle \;=\; -c(t)\,|\dot{\psi}(t)\rangle\;.} \tag{2.6}$$

Multiply by $\langle\psi(t)|$ we get a differential equation for $c(t)$:

$$\dot{c}(t) \;=\; -c(t)\;\langle\psi(t)|\dot{\psi}(t)\rangle\,, \tag{2.7}$$

which happily we can solve. Letting $c(t=0)=1$ we can write

$$c(t) = \exp\left(-\int_0^t\langle\psi(t')|\dot{\psi}(t')\rangle dt'\right)\,. \tag{2.8}$$

The above exponential is a phase because the bracket in the integrand is actually purely imaginary:

$$\begin{aligned}\langle\psi(t)|\dot{\psi}(t)\rangle &= \int dx\ \psi^*\frac{d\psi}{dt} = \int dx\ \frac{d}{dt}(\psi^*\psi) - \int dx\ \frac{d\psi^*}{dt}\psi \\ &= \frac{d}{dt}\int dx\ \psi^*\psi - \langle\dot{\psi}(t)|\psi(t)\rangle\end{aligned} \tag{2.9}$$

Since the wavefunction is normalized we have

$$\langle\psi(t)|\dot{\psi}(t)\rangle = -\langle\dot{\psi}(t)|\psi(t)\rangle = -\langle\psi(t)|\dot{\psi}(t)\rangle^* \tag{2.10}$$

showing that indeed $\langle\psi(t)|\dot{\psi}(t)\rangle$ is purely imaginary. To emphasize this fact we write

$$c(t) = \exp\left(i\int_0^t i\langle\psi(t')|\dot{\psi}(t')\rangle dt'\right) \tag{2.11}$$

Having apparently solved for $c(t)$ we now return to our ansatz (2.3), we get

$$\boxed{|\Psi(t)\rangle \simeq c(0)\exp\left(i\int_0^t i\langle\psi(t')|\dot{\psi}(t')\rangle dt'\right)\exp\left(\frac{1}{i\hbar}\int_0^t E(t')dt'\right)|\psi(t)\rangle\,.} \tag{2.12}$$

But there is a mistake in this analysis. We really did not solve the Schrödinger equation! That's why we put a $\simeq$ instead of an equality.

The equation we had to solve, (2.6), is a vector equation, and forming the inner product with $\langle\psi(t)|$ gives a necessary condition for the solution, but not a sufficient one. We must check the equation forming the overlap with a full basis set of states. Indeed since $|\psi(t)\rangle$ is known, the equation can only have a solution if the two vectors $|\dot{\psi}(t)\rangle$ and $|\psi(t)\rangle$ are parallel. This does not happen in general. So we really did not solve equation (2.6). The conclusion is that, ultimately, the ansatz in (2.3) is not good enough!

We can see the complication more formally. At $t = 0$ equation (2.6) reads

$$\dot{c}(0)|\psi(0)\rangle = -c(0)|\dot{\psi}(0)\rangle\,. \tag{2.13}$$

Using Gram-Schmidt we can construct an orthonormal basis $\mathcal{B}$ for the state space with the choice $|\psi(0)\rangle$ for the first basis vector:

$$\mathcal{B} = \left\{\ |1\rangle = |\psi(0)\rangle,\ |2\rangle,\ |3\rangle\,,\ldots\ \right\}. \tag{2.14}$$

Equation (2.13) requires

$$\langle n|\dot{\psi}(0)\rangle = 0 \qquad n = 2,\ 3,\ \ldots \tag{2.15}$$

This will not hold in general. The key insight, however, is that (2.12) is a fairly accurate solution if the Hamiltonian is slowly varying. Making the definitions:

$$\theta(t) \equiv -\frac{1}{\hbar}\int_0^t E(t')dt'\,, \qquad \nu(t) \equiv i\langle\psi(t)|\dot{\psi}(t)\rangle\,, \quad \gamma(t) \equiv \int_0^t \nu(t')dt' \tag{2.16}$$

so that θ, ν and γ are all real, the state reads

$$|\Psi(t)\rangle \simeq c(0)\exp\left(i\gamma(t)\right)\exp(i\theta(t))|\psi(t)\rangle\,. \tag{2.17}$$

The phase $\theta(t)$ is called the *dynamical* phase and the phase $\gamma(t)$ is called the *geometric phase*.

Comment: Instantaneous eigenstates are rather ambiguous. If one has the $|\psi(t)\rangle$, they can be modified by the multiplication by an arbitrary phase:

$$|\psi(t)\rangle \to |\psi'(t)\rangle = e^{-i\chi(t)}|\psi(t)\rangle\,. \tag{2.18}$$

3 Systematic approach

Must use a basis to see the error terms and get a more general picture. We will do this now systematically. But first let us state precisely the idea in adiabatic approximation. Consider a family of instantaneous eigenstates:

$$H(t)|\psi_n(t)\rangle = E_n(t)|\psi_n(t)\rangle \tag{3.1}$$

with $E_1(t) < E_2(t) < \ldots$, so that there are no degeneracies.
Adiabatic approximation: If at $t = 0$ $|\Psi(0)\rangle = |\psi_n(0)\rangle$ for some n, then if $H(t)$ is slowly varying for $0 \le t \le T$ then at time T we have $|\psi(T)\rangle \simeq |\psi_n(T)\rangle$ up to a calculable phase.

Key facts:

1. The probability to jump to another state $|\psi_k(t)\rangle$ with $k \neq n$ is highly suppressed.
2. The phases can sometimes be relevant and have geometric meaning. An overall phase cannot be observed but if we have a superposition

$$|\Psi(0)\rangle = c_1|\psi_1(0)\rangle + c_2|\psi_2(0)\rangle + \ldots \tag{3.2}$$

the relative phases acquired by $|\psi_1(0)\rangle$ and $|\psi_2(0)\rangle$ after time evolution can matter.

Calculation:

$$|\Psi(t)\rangle = \sum_n c_n(t)|\psi_n(t)\rangle \tag{3.3}$$

Schrödinger equation :

$$i\hbar \sum_n \left(\dot{c_n}|\psi_n(t)\rangle + c_n|\dot{\psi_n}(t)\rangle\right) = \sum_n c_n(t)E_n(t)|\psi_n(t)\rangle \tag{3.4}$$

act with $\langle\psi_k(t)|$ from the left:

$$\begin{aligned} i\hbar\dot{c_k} &= E_k c_k - i\hbar\sum_n \langle\psi_k|\dot{\psi_n}\rangle c_n \\ i\hbar\dot{c_k} &= \left(E_k - i\hbar\langle\psi_k|\dot{\psi_k}\rangle c_k\right) - i\hbar\sum_{n\neq k}\langle\psi_k|\dot{\psi_n}\rangle c_n \end{aligned} \tag{3.5}$$

We can relate $\langle\psi_k|\dot{\psi_n}\rangle$ to a matrix element of $H(t)$ in the space of instantaneous eigenvectors

$$H(t)|\psi_n\rangle = E_n(t)|\psi_n\rangle \tag{3.6}$$

take time derivative

$$\dot{H(t)}|\psi_n\rangle + H(t)|\dot{\psi_n}\rangle = \dot{E}_n(t)|\psi_n\rangle + E_n(t)|\dot{\psi_n}\rangle \tag{3.7}$$

multiplty by $\langle\psi_k(t)|$ with $k \neq n$

$$\langle\psi_k(t)|\dot{H(t)}|\psi_n\rangle + E_k(t)\langle\psi_k(t)|\dot{\psi_n}\rangle = \dot{E}_n(t)\langle\psi_k(t)|\dot{\psi_n}\rangle \tag{3.8}$$

hence

$$\langle\psi_k(t)|\dot{\psi_n}\rangle = \frac{\langle\psi_k(t)|\dot{H(t)}|\psi_n\rangle}{E_n(t) - E_k(t)} \equiv \frac{\dot{H}_{kn}}{E_n - E_k} \tag{3.9}$$

We can use plug (3.9) back in Eq.(3.5) to get

$$\boxed{i\hbar\dot{c_k} = \left(E_k - i\hbar\langle\psi_k|\dot{\psi_k}\rangle c_k\right) - i\hbar\sum_{n\neq k}\frac{\dot{H}_{kn}}{E_n - E_k}c_n} \tag{3.10}$$

Note that if the term proportional to $\frac{\dot{H}_{kn}}{E_n - E_k}$ vanishes, then $|c_k| = 1$, hence if you start in $|\psi_k\rangle$ you stay in $|\psi_k\rangle$.
If we ignore the extra term:

$$\begin{aligned} c_k(t) &= c_k(0)\exp\left[\frac{1}{i\hbar}\int_0^t \left(E_k(t') - i\hbar\langle\psi_k|\dot{\psi_k}\rangle\right)dt'\right] \\ &= c_k(0)\exp\left(\frac{1}{i\hbar}\int_0^t E_k(t')dt'\right)\exp\left(i\int_0^t i\langle\psi_k|\dot{\psi_k}\rangle dt'\right) \\ &= c_k(0)e^{i\theta_k(t)}e^{i\gamma_k(t)} \end{aligned} \tag{3.11}$$

where

$$\theta_k(t) = -\frac{1}{\hbar}\int_0^t E_k(t')dt' \tag{3.12}$$

$$\nu_k(t) = i\langle\psi_k(t)|\dot{\psi}_k(t)\rangle \tag{3.13}$$

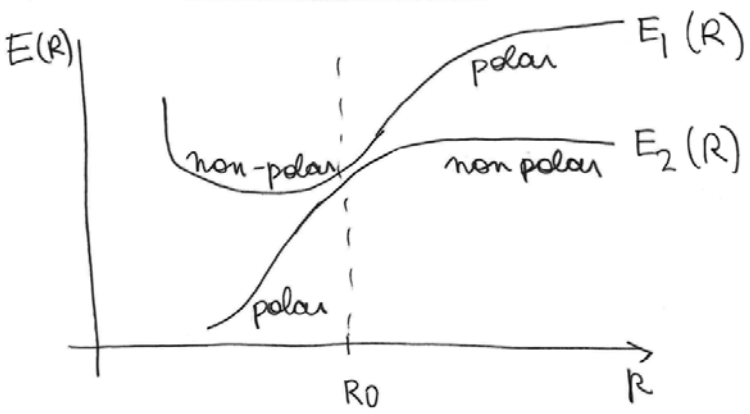
$$\gamma(t)_k = \int_0^t \nu_k(t')dt' \tag{3.14}$$

4 Landau-Zener transitions

Take $\psi_1(x;R)$ and $\psi_2(x;R)$ to be the electronic configurations of a molecule with fixed nuclei separated at a distance R.

We have

$$H(R)\psi_i(x;R) = E_i(R)\psi_i(x;R) \tag{4.1}$$



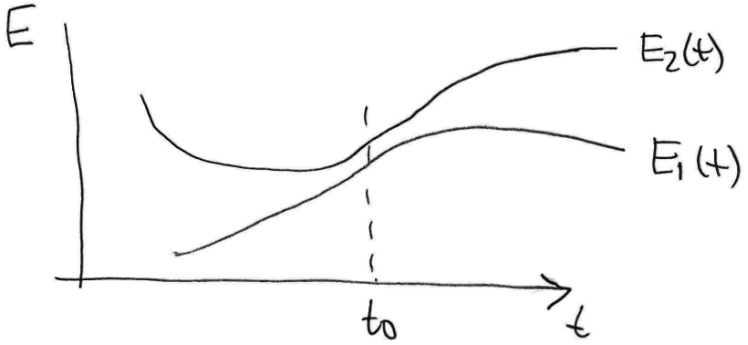
Depending on R the states are polar or non polar changing characteristic near $R = R_0$. If R changes slowly, ψ_1 remains ψ_1 or ψ_2 will remain ψ_2. But if R varies quickly, then $\psi_1 \to \psi_2$ near R_0. This would be a non-adiabatic transition.
Thinking of R as a function of time, we have a time dependent hamiltonian

$$H\big(R(t)\big)$$

with instantaneous energy eigenstates

$$\psi_i\big(x;R(t)\big)\,, \qquad E_i\big(R(t)\big)$$

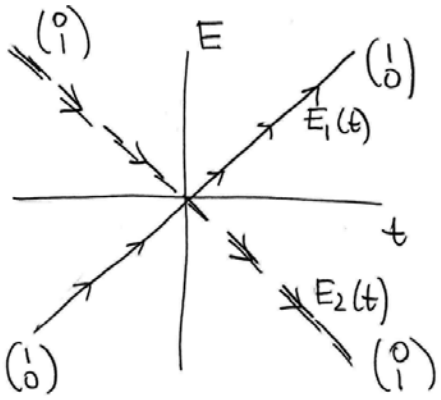
we can now plot the energies for constant velocity $\dot{R}$



We can sometimes think of this as a 2-level problem; if no other eigenstates are relevant.
So consider a slightly idealized 2×2 system

$$H(t) = \begin{pmatrix} \frac{\alpha t}{2} & 0 \\ 0 & -\frac{\alpha t}{2} \end{pmatrix}, \quad \alpha > 0 \qquad\qquad |1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{(spin up)}$$

$$E_1(t) = \frac{\alpha t}{2}\,, \quad E_2(t) = -\frac{\alpha t}{2} \qquad\qquad |2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad \text{(spin down)} \tag{4.2}$$



The instantaneous eigenstates $|1\rangle$, $|2\rangle$ are actually time independent. Take

$$|\psi_1\rangle = \begin{pmatrix}1\\0\end{pmatrix} \qquad |\psi_2\rangle = \begin{pmatrix}0\\1\end{pmatrix} \tag{4.3}$$

then

$$|\psi_1(t)\rangle = \exp\left(\frac{1}{i\hbar}\int_0^t E_1(t')dt'\right)|1\rangle = \exp\left(-\frac{i\alpha t^2}{4\hbar}\right)|1\rangle \quad \text{solves the Schrödinger equation} \tag{4.4}$$

$$|\psi_2(t)\rangle = \exp\left(\frac{1}{i\hbar}\int_0^t E_2(t')dt'\right)|2\rangle = \exp\left(+\frac{i\alpha t^2}{4\hbar}\right)|2\rangle \quad \text{solves the Schrödinger equation} \tag{4.5}$$

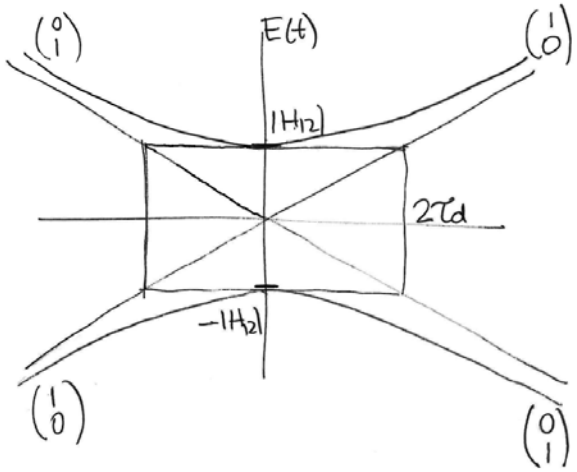
Time evolution is clear: if $|\psi\rangle = \begin{pmatrix}1\\0\end{pmatrix}$ at $t = -\infty$ it will remain in that state forever. Same for $|\psi\rangle = \begin{pmatrix}0\\1\end{pmatrix}$.

Now make the problem more interesting by perturbing the hamiltonian

$$H(t) = \begin{pmatrix}\frac{\alpha t}{2} & H_{12}\\ H_{12}^* & -\frac{\alpha t}{2}\end{pmatrix} \tag{4.6}$$

with H_{12} constant.

At $t = 0$ the energy eigenvalues are $\pm|H_{12}|$



$$H = \frac{\alpha t}{2}\sigma_z + \Re(H_{12})\sigma_x - \Im(H_{12})\sigma_y \tag{4.7}$$

$$E_\pm(t) = \pm\sqrt{|H_{12}|^2 + \frac{\alpha^2 t^2}{4}} \tag{4.8}$$

we can write H in a compact form by defining the vector

$$\mathbf{a} = \left(H_{12}, 0, \frac{\alpha t}{2}\right) = |\mathbf{a}|\mathbf{n} = E_+(t)\mathbf{n} \tag{4.9}$$

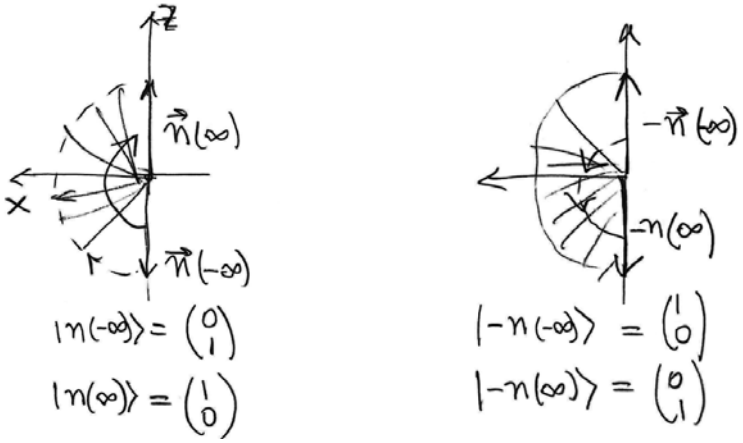
taking H_{12} to be real

so that

$$H = \mathbf{a}\cdot\boldsymbol{\sigma} \tag{4.10}$$

The instantaneous energy eigenstates are

$$\big|\pm\mathbf{n}(t)\big\rangle \quad \text{with energies} \quad E_\pm(t)$$



The instantaneous energy eigenstates change type

$$\begin{pmatrix}0\\1\end{pmatrix} \to \begin{pmatrix}1\\0\end{pmatrix} \qquad \text{(polar - non polar)}$$

$$\begin{pmatrix}1\\0\end{pmatrix} \to \begin{pmatrix}0\\1\end{pmatrix} \qquad \text{(non polar - polar)}$$

An adiabatic process will keep you there. Consider τ_d for the duration of the change $\frac{|H_{12}|}{|\alpha|} \equiv \tau_\alpha$, since

$$E_1 = \frac{\alpha t}{2} \to |H_{12}| = \frac{|\alpha| t}{2} \quad \text{(see fig)} \tag{4.11}$$

Also $\frac{|H_{12}|}{\hbar} \equiv \omega_{12}$ and it is called *Rabi frequency.* It's relevant for the transitions at $t = 0$ since $H(0) = \begin{pmatrix}0 & H_{12}\\ H_{12} & 0\end{pmatrix}$.

Process is adiabatic when

$$\boxed{\omega_{12}\tau_\alpha \gg 1} \implies \frac{|H_{12}|^2}{\hbar|\alpha|} \gg 1 \tag{4.12}$$

i.e.

$$\frac{2\pi}{\omega_{12}} = T_{12} \ll \tau_\alpha \tag{4.13}$$

hence, the adiabatic change is much slower than the natural time scale of the system.
Alternatively: The Hamiltonian should not vary much over the time scale T associated with the relevant energy difference ΔE

$$\left| T \frac{dH}{dt} \right| \ll H \tag{4.14}$$

Approximate $T = \frac{\hbar}{H}$ if $\Delta E \simeq H$

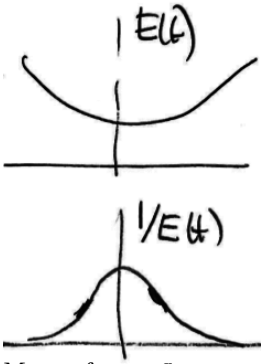
$$\left| \frac{\hbar}{H^2} \frac{dH}{dt} \right| \ll 1 \implies \left| \hbar \frac{d}{dt} \left(\frac{1}{H} \right) \right| \ll 1 \quad \text{or} \quad \left| \partial_t \left(\frac{\hbar}{E} \right) \right| \tag{4.15}$$

analog of $\left| \partial_x \left(\frac{\hbar}{p} \right) \right| \ll 1$ in WKB.
For our case

$$\left| \frac{d}{dt} \frac{\hbar}{\sqrt{|H_{12}|^2 + \frac{\alpha^2 t^2}{4}}} \right| \overset{?}{\ll} 1 \tag{4.16}$$

Let's check!

$$\begin{aligned} \left| \frac{d}{dt} \frac{\hbar}{\sqrt{|H_{12}|^2 + \frac{\alpha^2 t^2}{4}}} \right| &= \left| \frac{\hbar \alpha^2 t}{\left(|H_{12}|^2 + \frac{\alpha^2 t^2}{4} \right)^{3/2}} \right| = \hbar \alpha \left| \frac{\alpha t}{\left(|H_{12}|^2 + \frac{\alpha^2 t^2}{4} \right)^{3/2}} \right| \\ &\leq \max_t \ \hbar \alpha \left| \frac{\alpha t}{\left(|H_{12}|^2 + \frac{\alpha^2 t^2}{4} \right)^{3/2}} \right| \approx \frac{\hbar \alpha |H_{12}|}{|H_{12}|^3} = \frac{\hbar \alpha}{|H_{12}|^2} \ll 1 \quad \checkmark \end{aligned} \tag{4.17}$$



Max of $\frac{x}{(a^2+x^2)^{3/2}}$ happens for $x^2 = \frac{a^2}{2}$

Probability for a non-adiabatic transition

$$P_{n.ad.} = \exp\left(-2\pi \omega_{12} \tau_\alpha\right) = \exp\left(-2\pi \frac{|H_{12}|^2}{\hbar |\alpha|} \right) \tag{4.18}$$

5 Berry's phase

Adiabatic theorem: $|\psi(t=0)\rangle = |\psi_n(0)\rangle$ and with instantaneous eigenstates $|\psi_n(t)\rangle$ we find

$$|\psi(t)\rangle \simeq e^{i\theta_n(t)} e^{i\gamma_n(t)} |\psi_n(t)\rangle \tag{5.1}$$

with, as in (3.12)

$$\theta_n(t) = -\frac{1}{\hbar} \int_0^t E_n(t') dt' \tag{5.2}$$

$$\nu_n(t) = i \langle \psi_n(t) | \dot{\psi}_n(t) \rangle \tag{5.3}$$

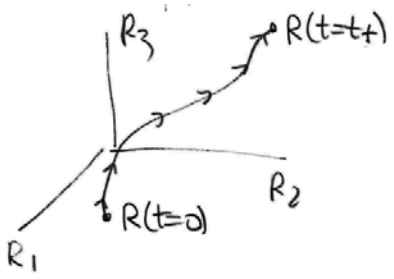
$$\gamma_n(t) = \int_0^t \nu_n(t') dt' \tag{5.4}$$

We now understand the relevance of $\gamma_n(t)$, the *geometrical phase*:

Assume H depends on a set of coordinates

$$\mathbf{R}(t) = (R_1(t),\, R_2(t), \ldots,\, R_N(t)) \tag{5.5}$$

several parameters that are tune dependent.



Instantaneous states

$$H(\mathbf{R})|\psi_n(\mathbf{R})\rangle = E(\mathbf{R})|\psi_n(\mathbf{R})\rangle \tag{5.6}$$

Evaluate the geometric phase. Start by computing

$$\nu_n(t) = i\ \psi_n(\mathbf{R}(t))\big|\frac{d}{dt}\big|\psi_n(\mathbf{R}(t))\big\rangle \tag{5.7}$$

we need $\frac{d}{dt}\big|\psi_n(\mathbf{R}(t))\big\rangle$

$$\frac{d}{dt}\big|\psi_n(\mathbf{R}(t))\big\rangle = \sum_{i=1}^{N} \frac{d}{d\mathbf{R}_i}\big|\psi_n(\mathbf{R}(t))\big\rangle \frac{d\mathbf{R}_i}{dt} = \vec{\nabla}_{\mathbf{R}}\big|\psi_n(\mathbf{R}(t))\big\rangle \cdot \frac{d\mathbf{R}(t)}{dt} \tag{5.8}$$

so that

$$\nu_n(t) = i\ \psi_n(\mathbf{R}(t))\big|\vec{\nabla}_{\mathbf{R}}\big|\psi_n(\mathbf{R}(t))\big\rangle \cdot \frac{d\mathbf{R}(t)}{dt} \tag{5.9}$$

and

$$\gamma_n(\tau) \equiv \int_0^\tau \nu_n(t)dt = \int_0^\tau i\ \psi_n(\mathbf{R}(t))\big|\vec{\nabla}_{\mathbf{R}}\big|\psi_n(\mathbf{R}(t))\big\rangle \cdot \frac{d\mathbf{R}(t)}{dt}dt \tag{5.10}$$

hence the geometrical phase $\gamma_n(t_f)$, also known as *Berry phase*, is

$$\boxed{\gamma_n(t_f) = \int_{\mathbf{R}_i}^{\mathbf{R}_f} i\ \psi_n(\mathbf{R})\big|\vec{\nabla}_{\mathbf{R}}\big|\psi_n(\mathbf{R})\big\rangle \cdot \mathrm{d}\mathbf{R}} \tag{5.11}$$

The integral depends on the path, but does not depend on time!! Whether you take a nano second or a year to make transition, the geometric phase is the same!

$i\ \psi_n(\mathbf{R})\big|\vec{\nabla}_{\mathbf{R}}\big|\psi_n(\mathbf{R})\big\rangle$ is an $N-$component object that lives in the parameter space. It is called the *Berry connection* $\mathbf{A}_n(\mathbf{R})$, associated with $|\psi_n(t)\rangle$

$$\mathbf{A}_n(\mathbf{R}) = i\ \psi_n(\mathbf{R})\big|\vec{\nabla}_{\mathbf{R}}\big|\psi_n(\mathbf{R})\big\rangle \tag{5.12}$$

In this way we can rewrite the Berry phase as

$$\gamma_n = \int_{\mathbf{R}_i}^{\mathbf{R}_f} \mathbf{A}_n(\mathbf{R}) \cdot \mathrm{d}\mathbf{R} \tag{5.13}$$

If we redefine the instantaneous states by an overall phase

$$\big|\psi_n(\mathbf{R})\big\rangle \to |\widetilde{\psi_n}(\mathbf{R})\rangle = e^{-i\beta(\mathbf{R})}\big|\psi_n(\mathbf{R})\big\rangle \tag{5.14}$$

where $\beta(\mathbf{R})$ is an arbitrary real function, what happens to $\mathbf{A}_n(\mathbf{R})$?

$$\begin{aligned}\widetilde{\mathbf{A}_n}(\mathbf{R}) &= i\ \widetilde{\psi_n}(\mathbf{R})\big|\vec{\nabla}_{\mathbf{R}}\big|\widetilde{\psi_n}(\mathbf{R})\big\rangle = \\ &= i\ \psi_n(\mathbf{R})\big|e^{i\beta(\mathbf{R})}\vec{\nabla}_{\mathbf{R}}e^{-i\beta(\mathbf{R})}\big|\psi_n(\mathbf{R})\big\rangle \\ &= i\left(-i\vec{\nabla}_{\mathbf{R}}\beta(\mathbf{R})\right)\underbrace{\langle\psi_n(\mathbf{R})|\psi_n(\mathbf{R})\rangle}_{1} + \mathbf{A}_n(\mathbf{R}) \qquad (5.15)\end{aligned}$$

$$\widetilde{\mathbf{A}_n}(\mathbf{R}) = \mathbf{A}_n(\mathbf{R}) + \vec{\nabla}_{\mathbf{R}}\beta(\mathbf{R}) \qquad (5.16)$$

analogous to the vector potential in EM ($\vec{A}' \to \vec{A}' + \nabla E$).
What about the Berry phase?

$$\widetilde{\gamma_n}(\mathbf{R}_f) = \int_{\mathbf{R}_i}^{\mathbf{R}_f}\widetilde{\mathbf{A}_n}(\mathbf{R})\cdot\mathrm{d}\mathbf{R} = \gamma_n(\mathbf{R}_f) + \int_{\mathbf{R}_i}^{\mathbf{R}_f}\vec{\nabla}_{\mathbf{R}}\beta(\mathbf{R})\cdot\mathrm{d}\mathbf{R} \implies \qquad (5.17)$$

$$\widetilde{\gamma_n}(\mathbf{R}_f) = \gamma_n(\mathbf{R}_f) + \beta(\mathbf{R}_f) - \beta(\mathbf{R}_i) \qquad (5.18)$$

The geometrical phase is completely well defined for closed paths in parameter space.
Comments:

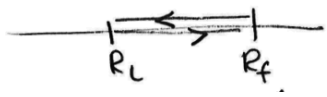
- If the $\psi_n(t)$ are real, then the Berry phase vanishes:

$$\begin{aligned}\nu_n &= i\langle\psi_n(t)|\dot{\psi}_n(t)\rangle = i\int d\mathbf{x}\,\psi_n^*(t,\mathbf{x})\frac{d}{dt}\psi_n(t,\mathbf{x}) \\ &= i\int d\mathbf{x}\,\psi_n(t,\mathbf{x})\frac{d}{dt}\psi_n(t,\mathbf{x}) = \frac{i}{2}\int d\mathbf{x}\,\frac{d}{dt}\Big(\psi_n(t,\mathbf{x})\Big)^2 = \\ &= \frac{i}{2}\frac{d}{dt}\int d\mathbf{x}\,|\psi_n(t,\mathbf{x})|^2 = 0\,, \qquad (5.19)\end{aligned}$$

  since the wavefunction is normalized. This should not be surprising. In general grounds we have seen that $\langle\psi_n(t)|\dot{\psi}_n(t)\rangle$ is purely imaginary. But if ψ_n is real this overlap cannot produce a complex number, so it can only be zero.

- If there is just one coordinate, i.e. $\mathbf{R} = R$, Berry's phase vanishes for a loop

$$\oint A_n(R)dR = 0 \qquad (5.20)$$



  In here the integral from R_i to R_f is cancelled by the integral back from R_f to R_i.

- In 3D we can make use of Stoke's theorem to simplify the calculation of $\gamma_n[C]$

$$\gamma_n[C] = \oint_C \mathbf{A}_n(\mathbf{R})\cdot\mathrm{d}\mathbf{R} = \iint_S\left(\vec{\nabla}\times\mathbf{A}_n(\mathbf{R})\right)\cdot d\vec{S} \equiv \iint_S \mathbf{D}_n\cdot d\vec{S} \qquad (5.21)$$

  where S is the surface with boundary C and we defined the *Berry curvature* $\mathbf{D}_n$

$$\mathbf{D}_n \equiv \vec{\nabla}\times\mathbf{A}_n(\mathbf{R}) \qquad (5.22)$$

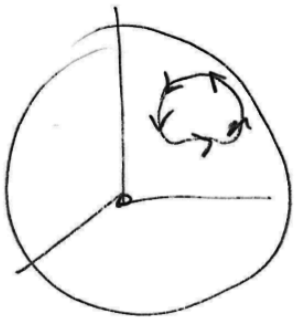
If we think of the Berry connection as the vector potential, the Berry curvature is the associated magnetic field. Note that the curvature is invariant under phase redefinition

$$\begin{aligned} \mathbf{D}_n \;\to\; \mathbf{D}'_n &= \;\vec{\nabla}\times\widetilde{\mathbf{A}_n}(\mathbf{R}) = \vec{\nabla}\times\Big(\mathbf{A}_n(\mathbf{R})+\vec{\nabla}\beta(\mathbf{R})\Big) \\ &= \;\vec{\nabla}\times\mathbf{A}_n(\mathbf{R}) + \cancel{\vec{\nabla}\times\vec{\nabla}\beta(\mathbf{R})} = \vec{\nabla}\times\mathbf{A}_n(\mathbf{R}) = \mathbf{D}_n\,. \end{aligned} \tag{5.23}$$

Example: Berry phase for an electron in a slowly varying magnetic field. Take a magnetic field with fixed intensity and slowly varying direction $\mathbf{B}(t) = B\vec{n}(t)$, put an electron inside this magnetic field, so that we get an interaction described by the hamiltonian

$$H(t) = -\boldsymbol{\mu}\cdot\mathbf{B}(t) = \mu_B B\vec{n}(t)\cdot\vec{\sigma} \tag{5.24}$$

The direction of the B field, $\vec{n}(t)$ swipes a closed loop C on the surface of an imaginary sphere of radius ρ in a time scale $T \gg \frac{\hbar}{\mu_B B}$. Think of the instantaneous eigenstates $\big|\chi_\pm\big(\mathbf{R}(t)\big)\big\rangle$ satisfying



$$H(t)\big|\chi_\pm\big(\mathbf{R}(t)\big)\big\rangle = \pm\mu_B B\big|\chi_\pm\big(\mathbf{R}(t)\big)\big\rangle \tag{5.25}$$

where

$$\mathbf{R}(t) = (\underbrace{r(t)}_{=\rho\text{ (fixed)}}, \theta(t)\,, \phi(t)) \tag{5.26}$$

We get

$$\vec{D}_\pm = \mp\frac{1}{2r^2}\hat{r} \implies \gamma_\pm[C] = \iint_S \vec{D}_\pm\cdot d\vec{S} = \mp\iint_S \frac{1}{2r^2}\hat{r}\cdot\hat{r}r^2 d\Omega = \mp\frac{1}{2}\iint_S d\Omega = \mp\frac{\Omega}{2} \tag{5.27}$$

6 Molecules and Born-Oppenheimer

Molecules are much harder to treat than atoms. Atoms are hard because even though the potential created by the nucleus is spherically symmetric, the Coulomb interactions between the electrons breaks the spherical symmetry. In molecules even ignoring Coulomb repulsion between electrons, the potential created by nuclei that are spatially separated is not spherically symmetric.

In some approximation one can view a molecule as a system in which nuclei in classical equilibrium with well localized positions while the electrons move around in the Coulomb potential created by the nuclei. This approximation is reasonable since typically $\frac{m}{M} \simeq 10^{-4}$ where m is the electron mass and M the nuclear one. In this picture slow nuclear vibrations adiabatically deform the electronic states.

In order to make estimates, consider a molecule of size a, so that

$$p_{\text{electron}} \sim \frac{\hbar}{a} \quad\text{and}\quad E_{\text{electron}} \sim \frac{\hbar^2}{ma^2} \tag{6.1}$$

The positively charged nuclei repell each other but the electrons in between create an effective attraction that, at equilibrium, cancels the repulsive forces. There will be nuclear vibrations around the equilibrium configuration. Consider the nuclear oscillations governed by the nuclear Hamiltonian

$$H_N \;=\; \frac{P^2}{2M} + \tfrac{1}{2}\,kx^2 \tag{6.2}$$

The restoring force is determined by k, and it is due to the electron system, with no reference to the mass M. Since k has units of energy over length-square, we must have

$$k \;=\; \frac{\text{Energy}}{L^2} \;\sim\; \frac{\hbar^2}{ma^4}\,. \tag{6.3}$$

But $k = M\omega^2$, with ω the frequency of nuclear oscillations so we have

$$M\omega^2 \sim \frac{\hbar^2}{ma^4} \quad\to\quad \omega^2 \sim \frac{m}{M}\frac{\hbar^2}{m^2a^4} \quad\to\quad \hbar\omega \sim \sqrt{\frac{m}{M}}\,\frac{\hbar^2}{ma^2}\,. \tag{6.4}$$

We thus find that the nuclear vibrational energies are

$$\boxed{E_{\text{vibration}} \;\sim\; \sqrt{\frac{m}{M}}E_{\text{electron}}\;.} \tag{6.5}$$

There are also rotations and their energy E_{rot} is even smaller, as they involve essentially no distortion of the molecule

$$E_{rot} = \frac{L^2}{2I} \simeq \frac{\hbar^2\ell(\ell+1)}{Ma^2} \sim \frac{m}{M}\frac{\hbar}{ma^2} \;\Longrightarrow\; \boxed{E_{\text{rotation}} \simeq \frac{m}{M}E_{\text{electron}}} \tag{6.6}$$

Therefore we have the following hierarchy of energies

$$E_{\text{electron}} \,:\, E_{\text{vibration}} \,:\, E_{\text{rotation}} \;=\; 1 \,:\, \sqrt{\frac{m}{M}} \,:\, \frac{m}{M}\,. \tag{6.7}$$

6.1 Born-Oppenheimer approximation

Consider a molecule with N nuclei and n electrons. The Hamiltonian takes the form

$$H = \sum_{\alpha=1}^{N}\frac{\mathbf{P}_\alpha^2}{2M_\alpha} + V_{NN}(\mathbf{R}) + \sum_{i=1}^{n}\frac{\mathbf{p}_i^2}{2m} + V_{eN}(\mathbf{R},\mathbf{r}) + V_{ee}(\mathbf{r})\,, \tag{6.8}$$

where M_α with $\alpha = 1,\ldots,N$ are the nuclear masses and

$\mathbf{P}_\alpha$, $\mathbf{R}_\alpha$: nuclei canonical variables	V_{NN} : nuclei-nuclei interaction
$\mathbf{p}_i$, $\mathbf{r}_i$: electron canonical variables	V_{ee} : electron-electron interaction
$\mathbf{R} \equiv (\mathbf{R}_1,\ldots,\mathbf{R}_N)$	V_{eN} : electron-nuclei interaction
$\mathbf{r} \equiv (\mathbf{r}_1,\ldots,\mathbf{r}_n)$	

The wavefunction $\psi(\mathbf{R},\mathbf{r})$ for the molecule is, in position space, a function of all the nuclear positions and all the electron positions.

In the limit when $M_\alpha/m \to \infty$ the nuclear skeleton may be considered fixed, making the positions $\mathbf{R}$ are fixed. The electrons then move under the effect of the nuclear potential $V_{eN}(\mathbf{R},\mathbf{r})$ with fixed $\mathbf{R}$, and the electron-electron Coulomb repulsion. The relevant Hamiltonian H_e for the electrons is then

$$H_e(\mathbf{p},\mathbf{r};\mathbf{R}) = \sum_{i=1}^{n}\frac{\mathbf{p}_i^2}{2m} + V_{eN}(\mathbf{R},\mathbf{r}) + V_{ee}(\mathbf{r})\,. \tag{6.9}$$

This is a different Hamiltonian each time we change the positions $\mathbf{R}$ of the nuclei. The associated Schrödinger equation for the electrons is

$$\left[-\frac{\hbar^2}{2m}\sum_{i=1}^{n}\nabla^2_{\mathbf{r}_i} + V_{eN}(\mathbf{R},\mathbf{r}) + V_{ee}(\mathbf{r})\right]\phi^{(i)}_{\mathbf{R}}(\mathbf{r}) = E^{(i)}_e(\mathbf{R})\phi^{(i)}_{\mathbf{R}}(\mathbf{r})\,. \tag{6.10}$$

The wavefunction for the electrons, as expected, is a function of the position of the electrons $\mathbf{r}$, which appears as the argument of the wavefunction. Since the wavefunction depends on the nuclear positions, this dependence is included as a subscript. Finally, the superscript i labels the various wavefunctions that may appear as solutions of this equation. The associated energies $E^{(i)}_e(\mathbf{R})$ depend on the nuclear positions and the label i. If we calculated all the $\phi^{(i)}_{\mathbf{R}}(\mathbf{r})$ we would have a full basis of electronic configurations and we could write an ansatz for the full wavefunction of the molecule:

$$\psi(\mathbf{R},\mathbf{r}) = \sum_i \eta^{(i)}(\mathbf{R})\phi^{(i)}_{\mathbf{R}}(\mathbf{r})\,, \tag{6.11}$$

where the $\eta^{(i)}$ are the unknowns. Substitution into the full Schrödinger equation

$$H\psi(\mathbf{R},\mathbf{r}) = E\psi(\mathbf{R},\mathbf{r})\,, \tag{6.12}$$

gives an infinite set of coupled differential equations for $\eta^{(i)}(\mathbf{R})$. This is too difficult, so we try to make do with a single term:

$$\psi(\mathbf{R},\mathbf{r}) = \eta(\mathbf{R})\phi_{\mathbf{R}}(\mathbf{r})\,, \tag{6.13}$$

where we would generally use for $\phi_{\mathbf{R}}(\mathbf{r})$ the ground state wavefunction for the electrons in the frozen nuclear potential. If we have this wavefunction for all $\mathbf{R}$, as we now assume, we also know the value $E_e(\mathbf{R})$ of the associated energy.

We will do a variational analysis. For this we will compute the expectation value $\langle\psi|H|\psi\rangle$ using $\psi(\mathbf{R},\mathbf{r}) = \eta(\mathbf{R})\phi_{\mathbf{R}}(\mathbf{r})$. We will then utilize the known $\phi_{\mathbf{R}}(\mathbf{r})$ to integrate the electronic dependence in the expectation value

$$\begin{aligned}\langle H\rangle &= \int \mathrm{d}\mathbf{R}d\mathbf{r}\ \psi^*(\mathbf{R},\mathbf{r})H\,\psi(\mathbf{R},\mathbf{r}) = \int \mathrm{d}\mathbf{R}d\mathbf{r}\ \eta^*(\mathbf{R})\phi^*_{\mathbf{R}}(\mathbf{r})H\,\eta(\mathbf{R})\phi_{\mathbf{R}}(\mathbf{r})\\ &= \int \mathrm{d}\mathbf{R}\ \eta^*(\mathbf{R})H_{\text{eff}}\,\eta(\mathbf{R})\,,\end{aligned} \tag{6.14}$$

thus discovering the effective Hamiltonian H_{eff} for the nuclear degrees of freedom. We begin the calculation by rewriting the original Hamiltonian:

$$H = \hat{H}_N + \hat{H}_e\,, \qquad \hat{H}_N = \sum_{\alpha=1}^{N}\frac{\mathbf{P}^2_\alpha}{2M_\alpha} + V_{NN}(\mathbf{R})\,. \tag{6.15}$$

As a warmup we calculate the expectation value of $\hat{H}_e$:

$$\begin{aligned}\langle H_e\rangle &= \int d\mathbf{R}\, d\mathbf{r}\, \eta^*(\mathbf{R})\phi^*_{\mathbf{R}}(\mathbf{r})\hat{H}_e\eta(\mathbf{R})\phi_{\mathbf{R}}(\mathbf{r}) \\ &= \int d\mathbf{R}\, \eta^*(\mathbf{R}) \underbrace{\left[\int d\mathbf{r}\, \phi^*_{\mathbf{R}}(\mathbf{r})\hat{H}_e\phi_{\mathbf{R}}(\mathbf{r})\right]}_{E_e(\mathbf{R})} \eta(\mathbf{R}) \\ &= \int d\mathbf{R}\, \eta^*(\mathbf{R})E_e(\mathbf{R})\eta(\mathbf{R})\,. \end{aligned} \tag{6.16}$$

This term has contributed to the effective nuclear Hamiltonian the value of the $\mathbf{R}$ dependent electron energy. Now the nuclear term

$$\begin{aligned}\left\langle \frac{\mathbf{P}_\alpha^2}{2M_\alpha}\right\rangle &= \frac{1}{2M_\alpha}\int d\mathbf{R}\, d\mathbf{r}\, \eta^*(\mathbf{R})\phi^*_{\mathbf{R}}(\mathbf{r})\mathbf{P}_\alpha\mathbf{P}_\alpha(\eta(\mathbf{R})\phi_{\mathbf{R}}(\mathbf{r})) \\ &= \frac{1}{2M_\alpha}\int d\mathbf{R}\, d\mathbf{r}\, \eta^*(\mathbf{R})\phi^*_{\mathbf{R}}(\mathbf{r})\mathbf{P}_\alpha\Big[\big(\mathbf{P}_\alpha\eta(\mathbf{R})\big)\phi_{\mathbf{R}}(\mathbf{r}) + \eta(\mathbf{R})\big(\mathbf{P}_\alpha\phi_{\mathbf{R}}(\mathbf{r})\big)\Big] \end{aligned} \tag{6.17}$$

We want to move $\phi^*_{\mathbf{R}}(\mathbf{r})$ closer to the other $\phi_{\mathbf{R}}(\mathbf{r})$ to be able to do the integrals. For that we use

$$\phi^*_{\mathbf{R}}(\mathbf{r})\mathbf{P}_\alpha = \mathbf{P}_\alpha\phi^*_{\mathbf{R}}(\mathbf{r}) - \big(\mathbf{P}_\alpha\phi^*_{\mathbf{R}}(\mathbf{r})\big)\,, \tag{6.18}$$

where in the last term, as indicated by the parenthesis, the derivation is acting only on the field $\phi^*_{\mathbf{R}}(\mathbf{r})$. Hence

$$\begin{aligned}\left\langle \frac{\mathbf{P}_\alpha^2}{2M_\alpha}\right\rangle = \frac{1}{2M_\alpha}\int d\mathbf{R}\, d\mathbf{r}\, \eta^*(\mathbf{R}) \Big\{&\mathbf{P}_\alpha\Big[\phi^*_{\mathbf{R}}(\mathbf{r})\big(\mathbf{P}_\alpha\eta(\mathbf{R})\big)\phi_{\mathbf{R}}(\mathbf{r}) + \phi^*_{\mathbf{R}}(\mathbf{r})\eta(\mathbf{R})\big(\mathbf{P}_\alpha\phi_{\mathbf{R}}(\mathbf{r})\big)\Big] \\ &- \big(\mathbf{P}_\alpha\phi^*_{\mathbf{R}}(\mathbf{r})\big)\Big[\big(\mathbf{P}_\alpha\eta(\mathbf{R})\big)\phi_{\mathbf{R}}(\mathbf{r}) + \eta(\mathbf{R})\big(\mathbf{P}_\alpha\phi_{\mathbf{R}}(\mathbf{r})\big)\Big]\Big\} \end{aligned} \tag{6.19}$$

We can now move in the $d\mathbf{r}$ integral

$$\begin{aligned}\left\langle \frac{\mathbf{P}_\alpha^2}{2M_\alpha}\right\rangle = \frac{1}{2M}\int d\mathbf{R}\, \eta^*(\mathbf{R}) \Big\{&\mathbf{P}_\alpha\Big[\mathbf{P}_\alpha\eta(\mathbf{R})\int d\mathbf{r}\, \phi^*_{\mathbf{R}}(\mathbf{r})\phi_{\mathbf{R}}(\mathbf{r}) + \eta(\mathbf{R})\int d\mathbf{r}\, \phi^*_{\mathbf{R}}(\mathbf{r})\mathbf{P}_\alpha\phi_{\mathbf{R}}(\mathbf{r})\Big] \\ &- \big(\mathbf{P}_\alpha\eta(\mathbf{R})\big)\int d\mathbf{r}\, \big(\mathbf{P}_\alpha\phi^*_{\mathbf{R}}(\mathbf{r})\big)\phi_{\mathbf{R}}(\mathbf{r}) + \eta(\mathbf{R})\int d\mathbf{r}\, \big(\mathbf{P}_\alpha\phi^*_{\mathbf{R}}(\mathbf{r})\big)\big(\mathbf{P}_\alpha\phi_{\mathbf{R}}(\mathbf{r})\big)\Big\} \end{aligned} \tag{6.20}$$

It is now convenient to define

$$\boxed{\mathbf{A}_\alpha(\mathbf{R}) \equiv i\hbar\int d\mathbf{r}\, \phi^*_{\mathbf{R}}(\mathbf{r})\nabla_{\mathbf{R}_\alpha}\phi_{\mathbf{R}}(\mathbf{r}) = -\int d\mathbf{r}\, \phi^*_{\mathbf{R}}(\mathbf{r})\mathbf{P}_\alpha\phi_{\mathbf{R}}(\mathbf{r})} \tag{6.21}$$

This is a Berry connection! We have a full Berry connection for each nucleus (thus the label α). The Berry connection arises from the electronic configuration. With this definition we have

$$\begin{aligned}\left\langle \frac{\mathbf{P}_\alpha^2}{2M_\alpha}\right\rangle &= \frac{1}{2M}\int d\mathbf{R}\, \eta^*(\mathbf{R})\Big\{\mathbf{P}_\alpha^2\eta(\mathbf{R}) - \mathbf{P}_\alpha\eta(\mathbf{R})A_\alpha(\mathbf{R}) - A_\alpha(\mathbf{R})\big(\mathbf{P}_\alpha\eta(\mathbf{R})\big) + \hbar^2\eta(\mathbf{R})\int d\mathbf{r}\, \big|\nabla_{\mathbf{R}_\alpha}\phi_{\mathbf{R}}(\mathbf{r})\big|^2\Big\} \\ &= \int d\mathbf{R}\, \eta^*(\mathbf{R})\left\{\frac{(\mathbf{P}_\alpha - \mathbf{A}_\alpha)^2}{2M_\alpha} - \frac{\mathbf{A}_\alpha^2}{2M_\alpha} + \frac{\hbar^2}{2M_\alpha}\int d\mathbf{r}\, \big|\nabla_{\mathbf{R}_\alpha}\phi_{\mathbf{R}}\big|^2\right\}\eta(\mathbf{R}) \end{aligned} \tag{6.22}$$

Hence

$$\left\langle \sum_\alpha \frac{\mathbf{P}_\alpha^2}{2M_\alpha} \right\rangle = \int d\mathbf{R}\, \eta^*(\mathbf{R}) \left[\sum_\alpha \frac{(\mathbf{P}_\alpha - \mathbf{A}_\alpha)^2}{2M_\alpha} - \sum_\alpha \frac{\mathbf{A}_\alpha^2}{2M_\alpha} + \sum_\alpha \frac{\hbar^2}{2M_\alpha} \int d\mathbf{r} \left| \nabla_{\mathbf{R}_\alpha} \phi_{\mathbf{R}} \right|^2 \right] \eta(\mathbf{R}) \quad (6.23)$$

so that the total expression reads

$$\begin{aligned} \langle H \rangle &= \left\langle \sum_\alpha \frac{\mathbf{P}_\alpha^2}{2M_\alpha} + V_{NN}(\mathbf{R}) + H_e \right\rangle = \\ &= \int d\mathbf{R}\, \eta^*(\mathbf{R}) \left[\sum_\alpha \frac{(\mathbf{P}_\alpha - \mathbf{A}_\alpha)^2}{2M_\alpha} + V_{NN}(\mathbf{R}) + E_e(\mathbf{R}) - \sum_\alpha \frac{\mathbf{A}_\alpha^2}{2M_\alpha} + \sum_\alpha \frac{\hbar^2}{2M_\alpha} \int d\mathbf{r} \left| \nabla_{\mathbf{R}_\alpha} \phi_{\mathbf{R}} \right|^2 \right] \eta(\mathbf{R}) \end{aligned} \quad (6.24)$$

and separating $\langle H \rangle$ in kinematics and potential term

$$\langle H \rangle = \int d\mathbf{R}\, \eta^*(\mathbf{R}) \left[\sum_\alpha \frac{(\mathbf{P}_\alpha - \mathbf{A}_\alpha)^2}{2M_\alpha} + U(\mathbf{R}) \right] \eta(\mathbf{R}) \quad (6.25)$$

we can read from (6.24) the effective potential $U(\mathbf{R})$

$$\boxed{U(\mathbf{R}) \equiv V_{NN}(\mathbf{R}) + E_e(\mathbf{R}) + \sum_\alpha \frac{\hbar^2}{2M_\alpha} \int d\mathbf{r} \left| \nabla_{\mathbf{R}_\alpha} \phi_{\mathbf{R}} \right|^2 - \sum_\alpha \frac{\mathbf{A}_\alpha^2(\mathbf{R})}{2M_\alpha}} \quad (6.26)$$

Since

$$\mathbf{P}_\alpha - \mathbf{A}_\alpha = \frac{\hbar}{i} \nabla_{\mathbf{R}_\alpha} - \mathbf{A}_\alpha = \frac{\hbar}{i} \left(\nabla_{\mathbf{R}_\alpha} - \frac{i}{\hbar} \mathbf{A}_\alpha \right) , \quad (6.27)$$

the Schrödinger equation for nuclear motion is

$$\left[- \sum_\alpha \frac{\hbar^2}{2M_\alpha} \left(\nabla_{\mathbf{R}_\alpha} - \frac{i}{\hbar} \mathbf{A}_\alpha \right)^2 + U(\mathbf{R}) \right] \eta(\mathbf{R}) = E \eta(\mathbf{R}) \quad (6.28)$$

Berry's phases are not there if $\phi_{\mathbf{R}}(\mathbf{r})$ can be chosen to be real (note that we still have the $\int d\mathbf{r} \left| \nabla_{\mathbf{R}_\alpha} \phi_{\mathbf{R}} \right|^2$ term). Lowest order Born-Oppenheimer:

$$H = - \sum_\alpha \frac{\hbar^2}{2M_\alpha} \nabla_{\mathbf{R}_\alpha}^2 + V_{NN}(\mathbf{R}) + E_e(\mathbf{R}) \quad (6.29)$$

6.2 Following the direct route

$$H = \hat{H}_N + \hat{H}_e = \hat{T}_N + \hat{V}_{NN} + \hat{H}_e \quad (6.30)$$

where

$$\hat{T}_N = \sum_\alpha \frac{\hbar^2}{2M_\alpha} \nabla_{\mathbf{R}_\alpha}^2 \quad (6.31)$$

$$\hat{H}_e \phi_{\mathbf{R}}^{(i)} = E_e(\mathbf{R})^{(i)} \phi_{\mathbf{R}}^{(i)} \quad (6.32)$$

and

$$\psi = \sum_i \eta^{(i)}(\mathbf{R})\phi^{(i)}_{\mathbf{R}}(\mathbf{r})\,. \tag{6.33}$$

Therefore the eigenvalue equation $H\psi = E\psi$ looks like

$$\begin{aligned} H\psi &= \sum_i \hat{T}_N \eta^{(i)}(\mathbf{R})\phi^{(i)}_{\mathbf{R}}(\mathbf{r}) + \sum_i \eta^{(i)}(\mathbf{R})\left(\hat{V}_{NN} + \hat{H}_e\right)\phi^{(i)}_{\mathbf{R}}(\mathbf{r}) \\ &= \sum_i (\hat{T}_N + \hat{V}_{NN} + E_e^{(i)}(\mathbf{R}))\eta^{(i)}(\mathbf{R})\phi^{(i)}_{\mathbf{R}}(\mathbf{r}) - \sum_i \sum_\alpha \frac{\hbar^2}{2M_\alpha}\left[2\big(\nabla_{\mathbf{R}_\alpha}\eta^{(i)}(\mathbf{R})\big)\big(\nabla_{\mathbf{R}_\alpha}\phi^{(i)}_{\mathbf{R}}(\mathbf{r})\big) + \eta^{(i)}(\mathbf{R})\nabla^2_{\mathbf{R}_\alpha}\phi^{(i)}_{\mathbf{R}}(\mathbf{r})\right] \\ &= E\sum_i \eta^{(i)}(\mathbf{R})\phi^{(i)}_{\mathbf{R}}(\mathbf{r}) \end{aligned} \tag{6.34}$$

We now multiply by $\int d\mathbf{r}\,\phi^{*(j)}_{\mathbf{R}}(\mathbf{r})$

$$\left[\hat{T}_N + \hat{V}_{NN} + E_e^{(i)}(\mathbf{R})\right]\eta^{(j)} = E\eta^{(j)} + \sum_{i,\alpha}\frac{\hbar^2}{2M_\alpha}\left[2\big(\nabla_{\mathbf{R}_\alpha}\eta^{(i)}\big)\int d\mathbf{r}\,\phi^{*(j)}_{\mathbf{R}}(\mathbf{r})\nabla_{\mathbf{R}_\alpha}\phi^{(i)}_{\mathbf{R}}(\mathbf{r}) + \eta^{(i)}\int d\mathbf{r}\phi^{*(j)}_{\mathbf{R}}(\mathbf{r})\nabla^2_{\mathbf{R}_\alpha}\phi^{(i)}_{\mathbf{R}}(\mathbf{r})\right] \tag{6.35}$$

Suppose there was no sum over "i", so that $j = i$

$$\begin{aligned} &\sum_\alpha \frac{\hbar^2}{2M_\alpha}\left[2\nabla_{\mathbf{R}_\alpha}\eta^{(i)}\frac{1}{i\hbar}A_\alpha(\mathbf{R}) + \eta^{(i)}\int d\mathbf{r}\phi^{*(j)}_{\mathbf{R}}(\mathbf{r})\nabla^2_{\mathbf{R}_\alpha}\phi^{(i)}_{\mathbf{R}}(\mathbf{r})\right] \\ &= \nabla_{\mathbf{R}_\alpha}\left(\eta^{(i)}\int d\mathbf{r}\phi^{*(j)}_{\mathbf{R}}(\mathbf{r})\nabla_{\mathbf{R}_\alpha}\phi^{(i)}_{\mathbf{R}}(\mathbf{r})\right) - (\nabla_{\mathbf{R}_\alpha}\eta^{(i)})\frac{1}{i\hbar}A_\alpha(\mathbf{R}) - \eta^{(i)}\int d\mathbf{r}\nabla_{\mathbf{R}_\alpha}\phi^{*(j)}_{\mathbf{R}}(\mathbf{r})\nabla_{\mathbf{R}_\alpha}\phi^{(i)}_{\mathbf{R}}(\mathbf{r}) = \\ &= \frac{i}{\hbar}P_\alpha\left(\eta^i\frac{1}{i\hbar}A_\alpha\right) - \cancel{(\nabla_{\mathbf{R}_\alpha}\eta^{(i)})\frac{1}{i\hbar}A_\alpha(\mathbf{R})} - \eta^{(i)}\int d\mathbf{r}\left|\nabla_{\mathbf{R}_\alpha}\phi^{(j)}_{\mathbf{R}}(\mathbf{r})\right|^2 \end{aligned} \tag{6.36}$$

Back

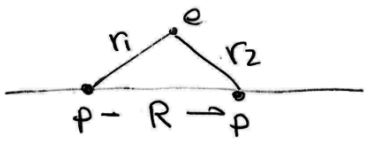
$$\sum_\alpha \frac{1}{2M_\alpha}P_\alpha\left(\eta^i A_\alpha\right) - A_\alpha\mathbf{P}_\alpha\eta^{(i)}\int -\eta^{(i)}\int d\mathbf{r}\left|\nabla_{\mathbf{R}_\alpha}\phi^{(j)}_{\mathbf{R}}(\mathbf{r})\right|^2 \tag{6.37}$$

would get perfect agreement!!

6.3 The H_2^+ ion

The electron Hamiltonian is

$$H_e = \underbrace{-\frac{\hbar^2}{2m}\nabla^2}_{\hat{T}_e}\underbrace{-e^2\left(\frac{1}{r_1} + \frac{1}{r_2}\right)}_{V_{Ne}} \tag{6.38}$$



Do a variational ansatz

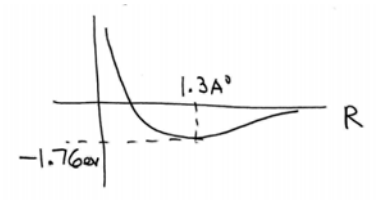
$$\psi = A[\psi_0(r_1) + \psi_0(r_2)] \qquad \psi_0(r) = \frac{1}{\sqrt{\pi a_0^3}}e^{-\frac{r}{a_0}} \tag{6.39}$$

Impose normalization of the wavefunction

$$|\psi|^2 = 1 \implies |A|^2 = \frac{1}{2(1+I)} \qquad \text{with} \quad I \equiv e^{\frac{R}{a}}\left[1 + \frac{R}{a} + \frac{1}{3}\left(\frac{R}{a}\right)^2\right] \tag{6.40}$$

Since $\langle H_e \rangle \simeq E_e(R)$ the full potential is

$$E_e(R) + \underbrace{V_{NN}(R)}_{\frac{e^2}{R}} \tag{6.41}$$



Experimentally we have $R = 1.06\mathring{A}$ and $E = -2.8$ eV.
Ansatz is not very accurate, for small R wavefunction becomes ground state of Hydrogen atom not ground state of Helium, as it should.

Chapter 7

Scattering

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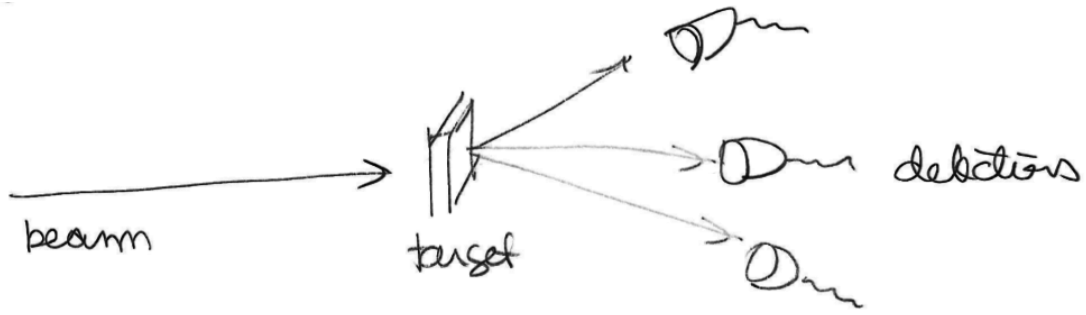
In high energy physics experiments a beam of particles hits a target composed of particles. By detecting the by-products one aims to study the interactions that occur during the collision.



Collisions can be rather intricate. For example, the particles involved may be not elementary (protons) or they may be elementary (electrons and positrons)

$$\begin{aligned} p + p &\rightarrow p + p + \pi^0 \\ p + p &\rightarrow p + n + \pi^+ \\ e^+ + e^- &\rightarrow \mu^+ + \mu^- \end{aligned}$$

The final products may not be the same as the initial particles. Some particles may be created.
Here collisions are like reactions in which

$$a + b \rightarrow c + d + e + \ldots$$

We have *scattering* when the particles in the initial and final state are the same

$$a + b \rightarrow a + b$$

The scattering is *elastic* if none of the particles internal states change in the collision[1]. We will focus on *elastic scattering* of particles *without spin* in the *nonrelativistic approximation.*

We will also assume that the interaction potential is translational invariant, that is, $V(\mathbf{r_1} - \mathbf{r_2})$. It follows that in the CM frame the problem reduces, as we did for hydrogen atom, to scattering of a single particle of reduced mass off a potential $V(\mathbf{r})$. We will work with energy eigenstates and we will not attempt to justify steps using wave-packets.

7.1 The Schrödinger equation for elastic scattering

We are interested in energy eigenstates

$$H = \frac{\mathbf{p}^2}{2M} + V(\mathbf{r}) \tag{7.1.1}$$

$$\psi(\mathbf{r}, t) = \psi(\mathbf{r}) e^{-\frac{iEt}{\hbar}} \tag{7.1.2}$$

$$\left[-\frac{\hbar^2}{2M} \nabla^2 + V(\mathbf{r}) \right] \psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{7.1.3}$$

Figure 7.1: Potential is finite range, or vanishes faster than $\frac{1}{r}$ as $r \to \infty$

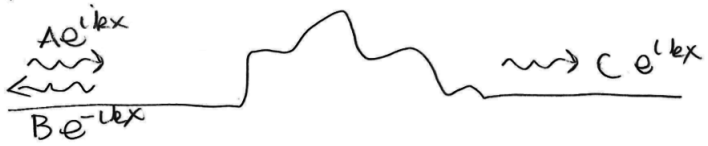
Will be consider solutions with positive energy. The energy is the energy of the particle far away from the potential, $E = \frac{\hbar^2 k^2}{2M}$. The Schrödinger equation then takes the form

$$\left[-\frac{\hbar^2}{2M} \left(\nabla^2 + k^2 \right) + V(\mathbf{r}) \right] \psi(\mathbf{r}) = 0 \tag{7.1.4}$$

Now we must set up the waves! Recall the 1D case. Physics dictates the existence of three waves: an incoming one, a reflected one, and a transmitted one. We can think of the reflected and transmitted waves as the scattered wave, the waves produced given the incoming wave. Setting up the waves is necessary in order to eventually solve the problem by looking into the details in the region where the potential is non-zero. When the potential has finite range the incoming and scattered waves are simple plane waves that are easily

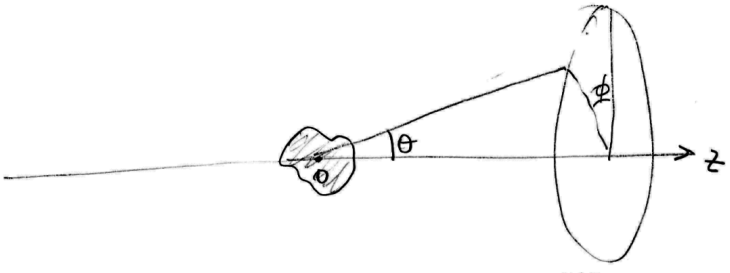
[1] Frank-Hertz experiment involved inelastic collisions of electrons with mercury atoms in which the mercury atoms are excited.

written.



Equation (7.1.4) has an inifinite degeneracy of energy eigenstates. When $V(\mathbf{r}) \equiv 0$, for example, $e^{i\mathbf{k}\cdot\mathbf{x}}$ for any $\mathbf{k}$ such that $\mathbf{k}\cdot\mathbf{k} = k^2$ is a solution. Assume an incident wave moving towards $+\hat{z}$. Then the wavefunction will look like

$$\varphi(\mathbf{r}) = e^{ikz} \tag{7.1.5}$$



If we assume $V(\mathbf{r})$ has a finite range a, this $\varphi(\mathbf{r})$ satisfies (7.1.4) for any $r > a$. For $r < a$, however, it does not satisfy the equation; $\varphi(\mathbf{r})$ is a solution everywhere only if the potential vanishes.

Given an incident wave we will also have a scattered wave. Could it be an $\psi(\mathbf{r}) = e^{ikr}$ that propagates radially out?

$$\left(\nabla^2 + k^2\right) e^{ikr} \neq 0 \qquad \text{fails badly for } r \neq 0\text{!!} \tag{7.1.6}$$

On the other hand

$$\left(\nabla^2 + k^2\right) \frac{e^{ikr}}{r} = 0 \qquad \text{for } r \neq 0\,. \tag{7.1.7}$$

This is consistent with the radial equation having a solution $u(r) = e^{irk}$ in the region where the potential vanishes. Recall that the full radial solution takes the form $u(r)/r$.
Can the scattered wave therefore be $\frac{e^{ikr}}{r}$? Yes, but this is not general enough. We need to introduce some angular dependence. Hence our ansatz for the scattered wave is

$$\psi_s(\mathbf{r}) = f_k(\theta,\phi)\frac{e^{ikr}}{r} \tag{7.1.8}$$

We expect the intensity of the scattered wave to depend on direction and the function $f_k(\theta,\phi)$ does that. We will see that ψ_s is only a solution for $r \gg a$, arbitrarily far.

Both the incident and the scattered wave must be present, hence the wavefunction is

$$\boxed{\psi(\mathbf{r}) = \psi_s(\mathbf{r}) + \varphi(\mathbf{r}) \simeq e^{ikz} + f_k(\theta,\phi)\frac{e^{ikr}}{r}\,, \quad r \gg a\,.} \tag{7.1.9}$$

As indicated this expression is only true far away from the scattering center. We physically expect $f_k(\theta,\phi)$ to be determined by $V(\mathbf{r})$. $f_k(\theta,\phi)$ is called the *scattering amplitude*.

We now relate $f_k(\theta,\phi)$ to cross section!!

$$d\sigma = \frac{\left[\begin{smallmatrix}\#\text{ particles scattered per unit time}\\ \text{into solid angle } d\Omega \text{ about } (\theta,\phi)\end{smallmatrix}\right]}{\left[\text{flux of incident particles} = \frac{\#\text{ particles}}{\text{area}\cdot\text{time}}\right]} \tag{7.1.10}$$

$d\sigma$ is called *differential cross section*, it's the area that removes from the incident beam the particles to be scattered into the solid angle $d\Omega$. Let us calculate the numerator and the denominator. First the denominator, which is the probability current:

$$\begin{smallmatrix}\text{Incident flux}\\ \text{in } e^{ikz}\end{smallmatrix} = \frac{\hbar}{m}\text{Im}\left[\psi^*\nabla\psi\right] = \frac{\hbar k}{m}\hat{z} \tag{7.1.11}$$

Intuitively, this can be calculated by multiplying the probability density $|e^{ikz}|^2 = 1$, by the velocity $\frac{p}{m} = \frac{\hbar k}{m}$. The result is again an incident flux equal in magnitude to $\frac{\hbar k}{m}$.

To calculate the numerator we first find the number of particles in the little volume of thickness dr and area $r^2 d\Omega$

$\mathrm{d}n =$ number of particles in this little volume

$$\mathrm{d}n = |\psi(\mathbf{r})|^2\,\mathrm{d}^3\mathbf{r} = \left|f_k(\theta,\phi)\frac{e^{ikr}}{r}\right|^2 r^2\mathrm{d}\Omega\,\mathrm{d}r = |f_k(\theta,\phi)|^2\,\mathrm{d}\Omega\,\mathrm{d}r \tag{7.1.12}$$

With velocity $v = \frac{\hbar k}{m}$ all these particles in the little volume will go cross out in time $\mathrm{d}t = \frac{\mathrm{d}r}{v}$, therefore the number of particles per unit time reads

$$\frac{dn}{dt} = |f_k(\theta,\phi)|^2\,\frac{\mathrm{d}\Omega\,\mathrm{d}r}{\frac{\mathrm{d}r}{v}} = \frac{\hbar k}{m}\,|f_k(\theta,\phi)|^2\,\mathrm{d}\Omega$$

Back in the formula for the cross section we get

$$\mathrm{d}\sigma = \frac{\frac{\hbar\cancel{k}}{\cancel{m}}\,|f_k(\theta,\phi)|^2\,\mathrm{d}\Omega}{\frac{\hbar\cancel{k}}{\cancel{m}}}$$

hence

$$\text{Differential cross section: } \boxed{\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = |f_k(\theta,\phi)|^2} \tag{7.1.13}$$

$$\text{Total cross section: } \boxed{\sigma = \int \mathrm{d}\sigma = \int |f_k(\theta,\phi)|^2\,\mathrm{d}\Omega} \tag{7.1.14}$$

7.2 Phase shifts

Assume $V(\mathbf{r}) = V(r)$, so that we are dealing with a central potential. First recall the description of a free particle in spherical coordinates. With

$$V = 0\,, \quad E = \frac{\hbar^2 k^2}{2m}\,, \quad \psi(\mathbf{r}) = \frac{u_{E\ell}(r)}{r} Y_{\ell m}(\Omega) \tag{7.2.1}$$

the Schrödinger equation for $u_{E\ell}$

$$\left(-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right) u_{E\ell}(r) = \frac{\hbar^2 k^2}{2m} u_{E\ell}(r)$$
$$\left(-\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{\ell(\ell+1)}{r^2}\right) u_{E\ell}(r) = k^2 u_{E\ell}(r)\,. \tag{7.2.2}$$

Now take $\rho = kr$, then (7.2.2) reads

$$\left(-\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} + \frac{\ell(\ell+1)}{\rho^2}\right) u_{E\ell}(\rho) = u_{E\ell}(\rho) \tag{7.2.3}$$

Since k^2 disappeared from the equation, the energy is not quantized. The solution to (7.2.3) is

$$u_{E\ell}(\rho) = A_\ell \rho j_\ell(\rho) + B_\ell\, \rho\, n_\ell(\rho) \quad \text{or} \quad u_{E\ell}(r) = A_\ell r j_\ell(kr) + B_\ell\, r\, n_\ell(kr) \tag{7.2.4}$$

where

$j_\ell(\rho)$ is the spherical Bessel function	$j_\ell(\rho)$ is non singular at the origin
$n_\ell(\rho)$ is the spherical Neumann function	$n_\ell(\rho)$ is singular at the origin

Both have finite limits as $\rho \to \infty$

$$\rho\, j_\ell(\rho) \to \sin\left(\rho - \frac{\ell\pi}{2}\right) \tag{7.2.5}$$
$$\rho\, n_\ell(\rho) \to -\cos\left(\rho - \frac{\ell\pi}{2}\right) \tag{7.2.6}$$

Now, with the plane wave a solution, we must have

$$e^{ikz} = e^{ikr\cos\theta} = \sum_{\ell=0}^{\infty} a_\ell P_\ell(\cos\theta) j_\ell(kr) \tag{7.2.7}$$

for some coefficients a_ℓ. Using

$$Y_{\ell,0}(\theta) = \sqrt{\frac{2\ell+1}{4\pi}} P_\ell(\cos\theta) \quad \text{and} \quad j_\ell(x) = \frac{1}{2i^\ell}\int_{-1}^{1} e^{ixu} P_\ell(u)\mathrm{d}u \tag{7.2.8}$$

it can be shown that

$$\boxed{e^{ikz} = \sqrt{4\pi}\sum_{\ell=0}^{\infty}\sqrt{2\ell+1}\, i^{\ell}\, Y_{\ell,0}(\theta) j_{\ell}(kr)\ .} \tag{7.2.9}$$

This is an incredible relation in which a plane wave is built by a linear superposition of spherical waves with all possible values of angular momentum! Each ℓ contribution is a *partial wave*. Each partial wave is an exact solution when $V = 0$.

We can see the spherical ingoing and outgoing waves in each partial wave by expanding (7.2.9) for large r:

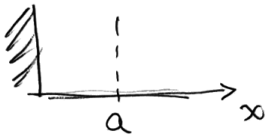
$$j_{\ell}(kr) \to \frac{1}{kr}\sin\left(kr - \frac{\ell\pi}{2}\right) = \frac{1}{2ik}\left[\frac{e^{i\left(kr-\frac{\ell\pi}{2}\right)}}{r} - \frac{e^{-i\left(kr-\frac{\ell\pi}{2}\right)}}{r}\right] \tag{7.2.10}$$

Thus

$$e^{ikz} = \frac{\sqrt{4\pi}}{k}\sum_{\ell=0}^{\infty}\sqrt{2\ell+1}\, i^{\ell}\, Y_{\ell,0}(\theta)\frac{1}{2i}\Big[\underbrace{\frac{e^{i\left(kr-\frac{\ell\pi}{2}\right)}}{r}}_{\text{outgoing}} - \underbrace{\frac{e^{-i\left(kr-\frac{\ell\pi}{2}\right)}}{r}}_{\text{incoming}}\Big], \quad r \gg a \tag{7.2.11}$$

7.2.1 Calculating the scattering amplitude in terms of phase shifts

Recall 1D case



$$\varphi(x) = \sin(kx) = \frac{1}{2i}\Big(e^{ikx} - \underbrace{e^{-ikx}}_{\text{ingoing}}\Big) \qquad \text{solution if } V = 0 \tag{7.2.12}$$

Exact solution

$$\psi(x) = \frac{1}{2i}\Big(e^{ikx}e^{2i\delta_k} - \underbrace{e^{-ikx}}_{\substack{\text{same}\\ \text{ingoing}\\ \text{wave}}}\Big) \qquad \text{for } x > a \tag{7.2.13}$$

where the outgoing wave can only differ from the ingoing one by a phase, so that probability is conserved. Finally we defined

$$\psi(x) = \psi_s(x) + \varphi(x) \tag{7.2.14}$$

So do a similar transformation to write a consistent ansatz for $\psi(\mathbf{r})$. We have from (7.1.9)

$$\psi(\mathbf{r}) \simeq e^{ikz} + f_k(\theta)\frac{e^{ikr}}{r}\,, \quad r \gg a\,. \tag{7.2.15}$$

The incoming partial waves in the left-hand side must be equal to the incoming partial waves in e^{ikz} since the scattered wave is outgoing. Introducing the phase shifts on the outgoing waves of the left-hand side we get

$$\psi(\mathbf{r}) = \frac{\sqrt{4\pi}}{k}\sum_{\ell=0}^{\infty}\sqrt{2\ell+1}\,i^{\ell}\,Y_{\ell,0}(\theta)\frac{1}{2i}\Big[\underbrace{\frac{e^{i\left(kr-\frac{\ell\pi}{2}\right)}e^{2i\delta_k}}{r}}_{\text{outgoing}} - \underbrace{\frac{e^{-i\left(kr-\frac{\ell\pi}{2}\right)}}{r}}_{\text{incoming}}\Big] \;=\; e^{ikz} + f_k(\theta)\frac{e^{ikr}}{r}$$

The incoming partial waves in e^{ikz} cancel in between the two sides of the equation, and moving the outgoing partial waves in e^{ikz} into the other side we get

$$\frac{\sqrt{4\pi}}{k}\sum_{\ell=0}^{\infty}\sqrt{2\ell+1}\,i^{\ell}\,Y_{\ell,0}(\theta)\,\underbrace{\frac{1}{2i}\left(e^{2i\delta_\ell}-1\right)}_{e^{i\delta_\ell}\sin\delta_\ell}\,\frac{e^{ikr}e^{-\frac{i\ell\pi}{2}}}{r} = f_k(\theta)\frac{e^{ikr}}{r} \tag{7.2.16}$$

$$= \frac{\sqrt{4\pi}}{k}\sum_{\ell=0}^{\infty}\sqrt{2\ell+1}\,Y_{\ell,0}(\theta)e^{i\delta_\ell}\sin\delta_\ell\,\frac{e^{ikr}}{r}\,, \tag{7.2.17}$$

where we noted that $e^{-\frac{i\ell\pi}{2}} = (-i)^{\ell}$ and $i^{\ell}(-i)^{\ell} = 1$. Therefore we get

$$\boxed{f_k(\theta) = \frac{\sqrt{4\pi}}{k}\sum_{\ell=0}^{\infty}\sqrt{2\ell+1}\,Y_{\ell,0}(\theta)e^{i\delta_\ell}\sin\delta_\ell\;.} \tag{7.2.18}$$

This is our desired expression for the scattering amplitude in terms of phase shifts.

We had

$$d\sigma = |f_k(\theta)|^2 d\Omega \tag{7.2.19}$$

and this differential cross section exhibits θ dependence. On the other hand for the full cross section the angular dependence, which is integrated over, must vanish

$$\sigma = \int |f_k(\theta)|^2\,\mathrm{d}\Omega = \int f_k^*(\theta)f_k(\theta)\mathrm{d}\Omega$$
$$= \frac{4\pi}{k^2}\sum_{\ell,\ell'}\sqrt{2\ell+1}\sqrt{2\ell'+1}\,e^{-i\delta_\ell}\sin\delta_\ell\,e^{i\delta_{\ell'}}\sin\delta_{\ell'}\underbrace{\int \mathrm{d}\Omega\,Y_{\ell,0}^*(\Omega)Y_{\ell',0}(\Omega)}_{\delta_{\ell\ell'}}$$

Hence

$$\boxed{\sigma = \frac{4\pi}{k^2}\sum_{\ell=0}^{\infty}(2\ell+1)\,\sin^2\delta_\ell\;.} \tag{7.2.20}$$

Now let us explore the form of $f(\theta)$ in the forward direction $\theta = 0$. Given that

$$Y_{\ell,0}(\theta) = \sqrt{\frac{2\ell+1}{4\pi}}P_\ell(\cos\theta) \quad\Longrightarrow\quad Y_{\ell,0}(\theta=0) = \sqrt{\frac{2\ell+1}{4\pi}}$$

then

$$f_k(\theta=0)=\frac{\sqrt{4\pi}}{k}\sum_{\ell=0}^{\infty}\sqrt{2\ell+1}\sqrt{\frac{2\ell+1}{4\pi}}e^{i\delta_\ell}\sin\delta_\ell=\frac{1}{k}\sum_{\ell=0}^{\infty}(2\ell+1)e^{i\delta_\ell}\sin\delta_\ell$$

Hence

$$\mathrm{Im}(f(0))=\frac{1}{k}\sum_{\ell=0}^{\infty}(2\ell+1)e^{i\delta_\ell}\sin^2\delta_\ell\ =\frac{1}{k}\frac{k^2}{4\pi}\sigma \tag{7.2.21}$$

Therefore we have found out a remarkable relation between the total elastic cross section and the imaginary part of the *forward* ($\theta=0$) *scattering amplitude*. This relation is known as the *Optical theorem* and reads

$$\boxed{\sigma=\frac{4\pi}{k}\mathrm{Im}(f(0))\ \ .} \qquad \text{Optical Theorem}$$

Let us consider ways in which we can identify the phase shifts δ_k. Consider a solution, restricted to a fixed ℓ

$$\psi(\mathbf{x})\Big|_\ell=\left(A_\ell j_\ell(kr)+B_\ell n_\ell(kr)\right)Y_{\ell,0}(\theta)\qquad x>a \tag{7.2.22}$$

If $B\neq 0$ then $V\neq 0$. As a matter of fact, if $V=0$ the solution should be valid everywhere and n_ℓ is singular at the origin, thus $B_\ell=0$.
Now, let's expand $\psi(\mathbf{x})|_\ell$ for large kr as in (7.2.10)

$$\psi(\mathbf{x})\Big|_\ell\simeq\left[\frac{A_\ell}{kr}\sin\left(kr-\frac{\ell\pi}{2}\right)-\frac{B_\ell}{kr}\cos\left(kr-\frac{\ell\pi}{2}\right)\right]Y_{\ell,0}(\theta) \tag{7.2.23}$$

Define

$$\tan\delta_\ell\equiv\ -\frac{B_\ell}{A_\ell} \tag{7.2.24}$$

We must now confirm that this agrees with the postulated definition as a relative phase between outgoing and ingoing spherical waves. We thus calculate

$$\begin{aligned}\psi(\mathbf{x})\Big|_\ell&\simeq\frac{1}{kr}\left[\sin\left(kr-\frac{\ell\pi}{2}\right)+\frac{\sin\delta_\ell}{\cos\delta_\ell}\cos\left(kr-\frac{\ell\pi}{2}\right)\right]Y_{\ell,0}(\theta)\\&\simeq\frac{1}{kr}\sin\left(kr-\frac{\ell\pi}{2}+\delta_\ell\right)Y_{\ell,0}(\theta) \qquad (7.2.25)\\&=\frac{1}{kr}\frac{1}{2i}\left[e^{i\left(kr-\frac{\ell\pi}{2}+\delta_\ell\right)}-e^{-i\left(kr-\frac{\ell\pi}{2}+\delta_\ell\right)}\right]Y_{\ell,0}(\theta)\\&\simeq e^{-i\delta}\frac{1}{kr}\frac{1}{2i}\left[e^{i\left(kr-\frac{\ell\pi}{2}+2\delta_\ell\right)}-e^{-i\left(kr-\frac{\ell\pi}{2}\right)}\right]Y_{\ell,0}(\theta) \qquad (7.2.26)\end{aligned}$$

This shows that our definition of δ_k above is indeed consistent the expansion in (7.2.16). Finally we can read the phase shift from (7.2.25)

$$\psi(\mathbf{x})\Big|_\ell \simeq \frac{1}{kr}\sin\left(kr - \frac{\ell\pi}{2} + \delta_\ell\right) Y_{\ell,0}(\theta) \qquad r \gg a \tag{7.2.27}$$

in the partial wave solution.

As an aside note that both the outgoing and ingoing components of a partial wave are separately acceptable asymptotic solutions obtained as:

- If $A_\ell = -iB_\ell$

$$\psi(\mathbf{x})\Big|_\ell \sim \left[i\sin\left(kr - \frac{\ell\pi}{2}\right) + \cos\left(kr - \frac{\ell\pi}{2}\right)\right]\frac{Y_{\ell,0}(\theta)}{kr} \sim \frac{e^{i\left(kr-\frac{\ell\pi}{2}\right)}}{kr}Y_{\ell,0}(\theta) \tag{7.2.28}$$

- If $A_\ell = iB_\ell$

$$\psi(\mathbf{x})\Big|_\ell \sim \frac{e^{-i\left(kr-\frac{\ell\pi}{2}\right)}}{kr}Y_{\ell,0}(\theta) \tag{7.2.29}$$

Each wave is a solution, but not a scattering one.

7.2.2 Example: hard sphere

$$V(r) = \begin{cases} \infty & r \le a \\ 0 & r > a \end{cases} \tag{7.2.30}$$

Radial solution

$$R_\ell(r) = \frac{u}{r} = A_\ell j_\ell(kr) + B_\ell n_\ell(kr) \tag{7.2.31}$$

$$\psi(a,\theta) = \sum_\ell R_\ell(a)P_\ell(\cos\theta) \equiv 0 \tag{7.2.32}$$

The $P_\ell(\cos\theta)$ are complete, meaning that

$$0 = R_\ell(a) = A_\ell j_\ell(ka) + B_\ell n_\ell(ka)\ \forall\,\ell \tag{7.2.33}$$

Recalling

$$\tan\delta_\ell \equiv -\frac{B_\ell}{A_\ell} = \frac{j_\ell(ka)}{n_\ell(ka)} \tag{7.2.34}$$

this implies all phase shifts are determined

$$\boxed{\tan\delta_\ell = \frac{j_\ell(ka)}{n_\ell(ka)}} \tag{7.2.35}$$

We can now easily compute the cross section σ, which, recalling (7.2.20) is proportional to $\sin^2\delta_\ell$

$$\sin^2\delta_\ell = \frac{\tan^2\delta_\ell}{1+\tan^2\delta_\ell} = \frac{j_\ell^2(ka)}{j_\ell^2(ka)+n_\ell^2(ka)} \tag{7.2.36}$$

hence

$$\sigma = \frac{4\pi}{k^2}\sum_{\ell=0}^{\infty}(2\ell+1)\,\sin^2\delta_\ell = \frac{4\pi}{k^2}\sum_{\ell=0}^{\infty}(2\ell+1)\,\frac{j_\ell^2(ka)}{j_\ell^2(ka)+n_\ell^2(ka)} \tag{7.2.37}$$

Griffiths gives you the low energy $ka \ll 1$ expansion

$$\sigma \simeq \frac{4\pi}{k^2}\sum_{\ell=0}^{\infty}\frac{1}{2\ell+1}\left[\frac{2^\ell \ell!}{(2\ell)!}\right]^4 (ka)^{4\ell+2} \tag{7.2.38}$$

At low energy the dominant contribution is from $\ell = 0$

$$\sigma \simeq \frac{4\pi}{k^2}(ka)^2 = 4\pi a^2 \qquad \begin{matrix}\text{Full area of the sphere!}\\ \text{Not the cross section!}\end{matrix} \tag{7.2.39}$$

One more calculation!

$$i\tan\delta = \frac{e^{i\delta}-e^{-i\delta}}{e^{i\delta}+e^{i\delta}} = \frac{e^{2i\delta}-1}{e^{2i\delta}+1} \qquad \Longrightarrow \qquad e^{2i\delta} = \frac{1+i\tan\delta}{1-i\tan\delta} \tag{7.2.40}$$

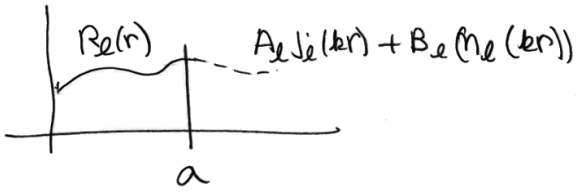
Therefore

$$e^{2i\delta_\ell} = \frac{1+i\frac{j_\ell(ka)}{n_\ell(ka)}}{1-i\frac{j_\ell(ka)}{n_\ell(ka)}} = \frac{n+ij}{n-ij} = \frac{i(j-in)}{-i(j+in)} \tag{7.2.41}$$

$$\boxed{e^{2i\delta_\ell} = \frac{j_\ell(ka)-in_\ell(ka)}{j_\ell(ka)+in_\ell(ka)}\,,} \qquad \begin{matrix}\text{Hard sphere}\\ \text{phase shifts}\end{matrix} \tag{7.2.42}$$

7.2.3 General computation of the phase shift

Suppose you have a radial solution $R_\ell(r)$ known for $r \le a$ ($V(r \ge a) = 0$). This must be matched to the general solution that holds for $V = 0$, as it holds for $r > a$:



At $r = a$ must match the function and its derivative

$$R_\ell(a) = A_\ell j_\ell(ka) + B_\ell n_\ell(ka) \tag{7.2.43}$$

$$aR'_\ell(a) = ka\Big(A_\ell j'_\ell(ka) + B_\ell n'_\ell(ka)\Big) \tag{7.2.44}$$

Let's form the ratio and define β_ℓ as the logarithmic derivative of the radial solution

$$\beta_\ell \equiv \frac{aR'_\ell(a)}{R_\ell(a)} = ka\frac{A_\ell j_\ell(ka) + B_\ell \eta'_\ell(ka)}{A_\ell j_\ell(ka) + B_\ell n_\ell(ka)} = ka\frac{j_\ell(ka) + \frac{B_\ell}{A_\ell}\eta'_\ell(ka)}{j_\ell(ka) + \frac{B_\ell}{A_\ell}n_\ell(ka)} = ka\frac{j_\ell(ka) - \tan\delta_\ell \eta'_\ell(ka)}{j_\ell(ka) - \tan\delta_\ell n_\ell(ka)} \tag{7.2.45}$$

In principle we can use eq. (7.2.45) to get $\tan\delta_\ell$, but let's push the calculation further to extract the phase shift from $e^{2i\delta_\ell}$

$$\begin{aligned}\beta_\ell &= ka\,\frac{j_\ell\cos\delta_\ell - \eta'_\ell\sin\delta_\ell}{j_\ell\cos\delta_\ell - n_\ell\sin\delta_\ell} = ka\,\frac{j_\ell\left(e^{i\delta_\ell}+e^{-i\delta_\ell}\right) + i\eta'_\ell\left(e^{i\delta_\ell}-e^{-i\delta_\ell}\right)}{j_\ell\left(e^{i\delta_\ell}+e^{-i\delta_\ell}\right) + in_\ell\left(e^{i\delta_\ell}-e^{-i\delta_\ell}\right)} \\ &= ka\,\frac{e^{i\delta_\ell}(j_\ell+i\eta'_\ell) + e^{-i\delta_\ell}(j_\ell - i\eta'_\ell)}{e^{i\delta_\ell}(j_\ell+in_\ell) + e^{-i\delta_\ell}(j_\ell - in_\ell)} = ka\,\frac{e^{2i\delta_\ell}(j_\ell+i\eta'_\ell) + (j_\ell - i\eta'_\ell)}{e^{2i\delta_\ell}(j_\ell+in_\ell) + (j_\ell - in_\ell)}\end{aligned} \tag{7.2.46}$$

Solve for $e^{2i\delta_\ell}$

$$e^{2i\delta_\ell} = -\frac{ka(j_\ell - i\eta'_\ell) - \beta_\ell(j_\ell - in_\ell)}{ka(j_\ell + i\eta'_\ell) - \beta_\ell(j_\ell + in_\ell)} \tag{7.2.47}$$

which can be rewritten as

$$\boxed{e^{2i\delta_\ell} = -\left(\frac{j_\ell - in_\ell}{j_\ell + in_\ell}\right)\left[\frac{\beta_\ell - ka\left(\frac{j_\ell - i\eta'_\ell}{j_\ell - in_\ell}\right)}{\beta_\ell - ka\left(\frac{j_\ell + i\eta'_\ell}{j_\ell + in_\ell}\right)}\right]} \tag{7.2.48}$$

which we can also write as

$$e^{2i\delta_\ell} = \underbrace{e^{2i\xi_\ell}}_{\substack{\text{Hard sphere}\\ \text{phase shift}}}\left[\frac{\beta_\ell - ka\left(\frac{j_\ell - i\eta'_\ell}{j_\ell - in_\ell}\right)}{\beta_\ell - ka\left(\frac{j_\ell + i\eta'_\ell}{j_\ell + in_\ell}\right)}\right] \tag{7.2.49}$$

Phase shifts are useful when a few of them dominate the cross section. This happens when $ka < 1$ with a the range of the potential. So short range and/or low energy.

1. Angular momentum of the incident particle is $L = b \cdot p$ with b impact parameter and p momentum

$$L \simeq bp \quad \to \quad \hbar\ell \simeq b\hbar k \quad \to \quad b \simeq \frac{\ell}{k} \tag{7.2.50}$$

When $b > a$ there is no scattering

$$\frac{\ell}{k} > a \qquad \boxed{\text{Expect no scattering for } \ell > ka} \tag{7.2.51}$$

Thus only values $\ell \leq ka$ contribute to σ.

2. Confirm the impact parameter intuition from partial wave expression. Consider the free partial wave $\sim j_\ell(kr)Y_{\ell,0}$. The impact parameter b_ℓ of such a wave would be estimated to be ℓ/k.

   Recall that $j_\ell(kr)$ is a solution of the $V = 0$ radial equation with angular momentum ℓ and energy $\hbar^2k^2/(2m)$. Setting the effective potential equal to the energy:

$$\frac{\hbar^2\ell(\ell+1)}{2mr^2} = \frac{\hbar^2k^2}{2m} \tag{7.2.52}$$

   we find that the turning point for the solution is at

$$k^2r^2 = \ell(\ell+1)\,. \tag{7.2.53}$$

   Thus we expect $j_\ell(kr)$ to be exponentially small beyond the turning point

$$kr \leq \sqrt{\ell(\ell+1)} \simeq \ell \tag{7.2.54}$$

   confirming that the wave is negligible for r less than the impact parameter ℓ/k!

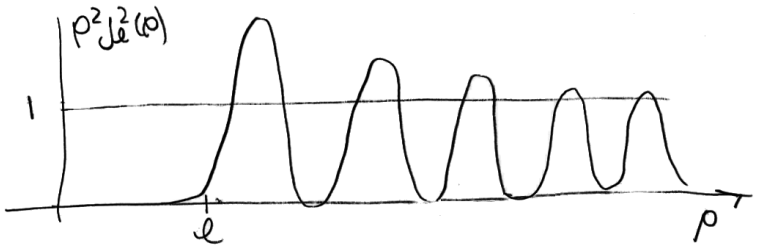


Figure 7.2: Plot of $\rho^2 J^2{}_\ell\,(\rho)$

7.3 Integral scattering equation

Some useful approximations can be made when we reformulate the time-independent Schrödinger equation as an integral equation. These approximations, as opposed to the partial waves method, allow us to deal with potentials that are not spherically symmetric. We consider the Schrödinger equation

$$\left[-\frac{\hbar^2}{2M}\nabla^2 + V(\mathbf{r})\right]\psi(\mathbf{r}) = E\psi(\mathbf{r})\,, \tag{7.3.1}$$

set the energy equal to that of a plane wave of wavenumber k and rewrite the potential in terms of a rescaled version $U(\mathbf{r})$ that simplifies the units:

$$E = \frac{\hbar^2 k^2}{2M} \quad \text{and} \quad V(\mathbf{r}) = \frac{\hbar^2}{2M} U(\mathbf{r}) \tag{7.3.2}$$

then the Schrödinger equation reads

$$\left[-\nabla^2 + U(\mathbf{r})\right] \psi(\mathbf{r}) = k^2 \psi(\mathbf{r}) \tag{7.3.3}$$

rewrite as

$$\left(\nabla^2 + k^2\right) \psi(\mathbf{r}) = U(\mathbf{r}) \psi(\mathbf{r}) \tag{7.3.4}$$

This is the equation we want to solve.

Let us introduce $G(\mathbf{r} - \mathbf{r}')$, a Green function for the operator $\nabla^2 + k^2$, i.e.

$$\left(\nabla^2 + k^2\right) G(\mathbf{r} - \mathbf{r}') = \delta^{(3)}(\mathbf{r} - \mathbf{r}') \tag{7.3.5}$$

Then we claim that any solution of the integral equation

$$\psi(\mathbf{r}) = \psi_0(\mathbf{r}) + \int \mathrm{d}^3\mathbf{r}' G(\mathbf{r} - \mathbf{r}') U(\mathbf{r}') \psi(\mathbf{r}') \tag{7.3.6}$$

where $\psi_0(\mathbf{r})$ is a solution of the homogeneus equation

$$\left(\nabla^2 + k^2\right) \psi_0(\mathbf{r}) = 0 \tag{7.3.7}$$

is a solution of equation (7.3.4). Let's check that this is true

$$\begin{aligned} \left(\nabla_{\mathbf{r}}^2 + k^2\right) \psi(\mathbf{r}) &= \left(\nabla_{\mathbf{r}}^2 + k^2\right) \int \mathrm{d}^3\mathbf{r}' G(\mathbf{r} - \mathbf{r}') U(\mathbf{r}') \psi(\mathbf{r}') \\ &= \int \mathrm{d}^3\mathbf{r}' \delta^{(3)}(\mathbf{r} - \mathbf{r}') U(\mathbf{r}') \psi(\mathbf{r}') \\ &= U(\mathbf{r}) \psi(\mathbf{r}) \qquad \checkmark \end{aligned} \tag{7.3.8}$$

To find G we first recall that

$$G(\mathbf{r}) \sim \begin{cases} \frac{C e^{\pm ikr}}{r} & \text{for } r \neq 0 \quad \text{as a matter of fact} \quad \left(\nabla_{\mathbf{r}}^2 + k^2\right) \frac{e^{\pm ikr}}{r} = 0 \quad \forall\, r \neq 0 \\ -\frac{1}{4\pi r} & \text{for } r \to 0 \quad \text{as a matter of fact} \quad \nabla^2 \left(-\frac{1}{4\pi r}\right) = \delta^3(\mathbf{r}) \end{cases} \tag{7.3.9}$$

Thus try

$$\boxed{G_{\pm}(\mathbf{r}) = -\frac{1}{4\pi} \frac{e^{\pm ikr}}{r}} \tag{7.3.10}$$

and we are going to refer to G_+ as the *outgoing wave* Green function and to G_- as the *ingoing wave* Green function.
Let's verify that this works, write G as a product: $G_\pm(r) = e^{\pm ikr}\left(-\frac{1}{4\pi r}\right)$, so that

$$\nabla^2 G_\pm(r) \;=\; \left(\nabla^2 e^{\pm ikr}\right)\left(-\frac{1}{4\pi r}\right) \;+\; e^{\pm ikr}\nabla^2\left(-\frac{1}{4\pi r}\right) \;+\; 2\left(\vec{\nabla}e^{\pm ikr}\right)\cdot\vec{\nabla}\left(-\frac{1}{4\pi r}\right) \tag{7.3.11}$$

Recall that

$$\nabla^2 = \nabla\cdot\nabla\,, \qquad \nabla r = \frac{\mathbf{r}}{r}\,, \qquad \nabla\cdot(f\mathbf{A}) = \nabla f\cdot\mathbf{A} + f\nabla\cdot\mathbf{A} \tag{7.3.12}$$

Therefore

$$\nabla e^{\pm ikr} = \pm ik\frac{\mathbf{r}}{r}e^{\pm ikr}\,, \qquad \nabla^2 e^{\pm ikr} = \left(-k^2 \pm \frac{2ik}{r}\right)e^{\pm ikr} \tag{7.3.13}$$

then

$$\begin{aligned}\nabla^2 G_\pm(r) &= \left(-k^2 \pm \frac{2ik}{r}\right)e^{\pm ikr}\left(-\frac{1}{4\pi r}\right) + e^{\pm ikr}\delta^3(\mathbf{r}) + 2\left(\pm ike^{\pm ikr}\frac{\mathbf{r}}{r}\right)\cdot\left(\frac{\mathbf{r}}{4\pi r^3}\right)\\ &= -k^2 G_\pm(r) \mp \cancel{\frac{2ik}{4\pi r}e^{\pm ikr}} + \delta^3(\mathbf{r}) \pm \cancel{\frac{2ik}{4\pi r}e^{\pm ikr}}\\ &= -k^2 G_\pm(r) + \delta^3(\mathbf{r}) \qquad \checkmark\end{aligned} \tag{7.3.14}$$

We will use

$$\psi_0(\mathbf{r}) = e^{ikz} \qquad \text{and} \qquad G = G_+ \tag{7.3.15}$$

Thus, with these choices, (7.3.6) takes the form

$$\psi(\mathbf{r}) = e^{ikz} + \int \mathrm{d}^3\mathbf{r}' G_+(\mathbf{r}-\mathbf{r}')U(\mathbf{r}')\psi(\mathbf{r}') \tag{7.3.16}$$

where

$$G_+(\mathbf{r}-\mathbf{r}') = -\frac{1}{4\pi}\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} \tag{7.3.17}$$

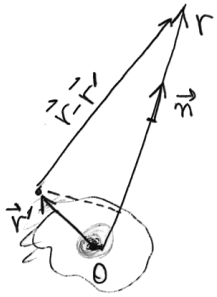
We now want to show that this is consistent with our asymptotic expansion for the energy eigenstates. For that we can make the following approximations

$$\text{For the } G_+ \text{ denominator:} \qquad |\mathbf{r}-\mathbf{r}'| \simeq r \tag{7.3.18}$$

$$\text{For the } G_+ \text{ numerator:} \qquad |\mathbf{r}-\mathbf{r}'| \simeq r - \mathbf{n}\cdot\mathbf{r}' \tag{7.3.19}$$

where

$$\mathbf{n} \equiv \frac{\mathbf{r}}{r}$$



In this way

$$G_+(\mathbf{r}-\mathbf{r}') = -\frac{1}{4\pi r} e^{ikr} e^{-ik\mathbf{n}\cdot\mathbf{r}'} \tag{7.3.20}$$

Thus

$$\psi(\mathbf{r}) = e^{ikz} + \left[-\frac{1}{4\pi}\int \mathrm{d}^3\mathbf{r}' e^{-ik\mathbf{n}\cdot\mathbf{r}'} U(\mathbf{r}')\psi(\mathbf{r}')\right]\frac{e^{ikr}}{r} \tag{7.3.21}$$

The object in brackets is a function of the unit vector $\mathbf{n}$ in the direction of $\mathbf{r}$. This shows that the integral equation, through the choice of G, incorporates both the Schrödinger equation and the asymptotic conditions. By definition, the object in brackets is $f_k(\theta,\phi)$, i.e.

$$f_k(\theta,\phi) = -\frac{1}{4\pi}\int \mathrm{d}^3\mathbf{r}' e^{-ik\mathbf{n}\cdot\mathbf{r}'} U(\mathbf{r}')\psi(\mathbf{r}')\,. \tag{7.3.22}$$

Of course, this does not yet determine f_k as the undetermined wavefunction $\psi(\mathbf{r})$ still appears under the integral. The incident wave has the form of $e^{i\mathbf{k_i}\cdot\mathbf{r}}$ with $\mathbf{k_i}$ the incident wave number, $|\mathbf{k_i}| = k$. For the outgoing wave we define $\mathbf{k_s} \equiv \mathbf{n}k$ (in the direction of $\mathbf{n}$), the scattered wave vector. The expression for $\psi(\mathbf{r})$ then becomes

$$\psi(\mathbf{r}) = e^{i\mathbf{k}_i\cdot\mathbf{r}} + \left[-\frac{1}{4\pi}\int \mathrm{d}^3\mathbf{r}' e^{-i\mathbf{k}_s\cdot\mathbf{r}'} U(\mathbf{r}')\psi(\mathbf{r}')\right]\frac{e^{ikr}}{r} \tag{7.3.23}$$

We will do better with the Born approximation.

7.3.1 The Born approximation

Consider the original integral expression:

$$\psi(\mathbf{r}) = e^{i\mathbf{k_i}\cdot\mathbf{r}} + \int \mathrm{d}^3\mathbf{r}' G_+(\mathbf{r}-\mathbf{r}')U(\mathbf{r}')\psi(\mathbf{r}') \tag{7.3.24}$$

Rewrite by just relabeling $\mathbf{r} \to \mathbf{r}'$

$$\psi(\mathbf{r}') = e^{i\mathbf{k_i}\cdot\mathbf{r}'} + \int \mathrm{d}^3\mathbf{r}'' G_+(\mathbf{r}'-\mathbf{r}'')U(\mathbf{r}'')\psi(\mathbf{r}'')\,. \tag{7.3.25}$$

Now plug (7.3.25) under the integral in (7.3.24) to get

$$\psi(\mathbf{r}) = e^{i\mathbf{k_i}\cdot\mathbf{r}} + \int \mathrm{d}^3\mathbf{r}' G_+(\mathbf{r}-\mathbf{r}')U(\mathbf{r}')e^{i\mathbf{k_i}\cdot\mathbf{r}'} + \int \mathrm{d}^3\mathbf{r}' G_+(\mathbf{r}-\mathbf{r}')U(\mathbf{r}')\int \mathrm{d}^3\mathbf{r}'' G_+(\mathbf{r}'-\mathbf{r}'')U(\mathbf{r}'')\psi(\mathbf{r}'') \tag{7.3.26}$$

Repeat the trick once more to find

$$\begin{aligned}\psi(\mathbf{r}) = e^{i\mathbf{k_i}\cdot\mathbf{r}} &+ \int \mathrm{d}^3\mathbf{r}' G_+(\mathbf{r}-\mathbf{r}')\,U(\mathbf{r}')e^{i\mathbf{k_i}\cdot\mathbf{r}'} \\ &+ \int \mathrm{d}^3\mathbf{r}' G_+(\mathbf{r}-\mathbf{r}')U(\mathbf{r}')\int \mathrm{d}^3\mathbf{r}'' G_+(\mathbf{r}'-\mathbf{r}'')\,U(\mathbf{r}'')e^{i\mathbf{k_i}\cdot\mathbf{r}''} \\ + \int \mathrm{d}^3\mathbf{r}' G_+(\mathbf{r}-\mathbf{r}')U(\mathbf{r}')\int \mathrm{d}^3\mathbf{r}'' G_+(\mathbf{r}'-\mathbf{r}'')U(\mathbf{r}'')&\int \mathrm{d}^3\mathbf{r}''' G_+(\mathbf{r}'''-\mathbf{r}'')U(\mathbf{r}''')\psi(\mathbf{r}''')\end{aligned} \tag{7.3.27}$$

By iterating this procedure we can form an infinite series which schematically looks like

$$\psi = e^{i\mathbf{k}_i\cdot\mathbf{r}} + \int GUe^{i\mathbf{k_i}\mathbf{r}} + \int GU\int GUe^{i\mathbf{k_i}\mathbf{r}} + \int GU\int GU\int GUe^{i\mathbf{k_i}\mathbf{r}} + \dots \quad (7.3.28)$$

The approximation in which we keep the first integral in this series and set to zero all others is called the *first Born approximation*. The preparatory work was done in (7.3.23), so we have now

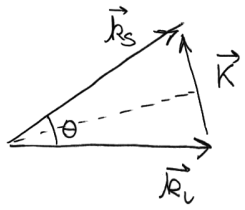
$$\psi^{\text{Born}}(\mathbf{r}) = e^{i\mathbf{k_i}\cdot\mathbf{r}} - \frac{1}{4\pi}\left(\int \mathrm{d}^3\mathbf{r}' e^{-i\mathbf{k_s}\cdot\mathbf{r}'}U(\mathbf{r}')e^{i\mathbf{k_i}\cdot\mathbf{r}'}\right)\frac{e^{ikr}}{r} \quad (7.3.29)$$

hence

$$\boxed{f_k^{\text{Born}}(\theta,\phi) = -\frac{1}{4\pi}\int \mathrm{d}^3\mathbf{r}e^{-i\boldsymbol{K}\cdot\mathbf{r}}U(\mathbf{r})\,.} \quad (7.3.30)$$

Here we defined the *wave-number transfer* $\boldsymbol{K}$:

$$|\mathbf{k_i}| = |\mathbf{k_s}|\,, \qquad \boldsymbol{K} \equiv \mathbf{k_s} - \mathbf{k_i} \quad (7.3.31)$$



Note that we eliminated the primes on the variable of integration – it is a dummy variable after all. The *wave-number transfer* is the momentum that must be added to the incident one to get the scattered one. We call θ the angle between $\mathbf{k_i}$ and $\mathbf{k_s}$ (it is the spherical angle θ if $\mathbf{k_i}$ is along the positive z-axis).
Note that

$$K = |\boldsymbol{K}| = 2k\sin\tfrac{\theta}{2} \quad (7.3.32)$$

In the Born approximation the scattering amplitude $f_k(\theta,\phi)$ is simply the Fourier transform of $U(\mathbf{r})$ evaluated at the momentum transfer $\boldsymbol{K}$! $f_k(\theta,\phi)$ captures some information of $V(\mathbf{r})$.

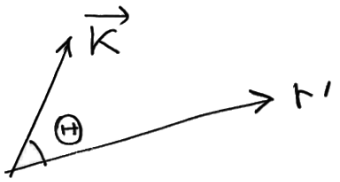
If we have a central potential $V(\mathbf{r}) = V(r)$, we can simplify the expression for the Born scattering amplitude further by performing the radial integration. We have

$$f_k^{\text{Born}}(\theta) = -\frac{1}{4\pi}\frac{2m}{\hbar^2}\int \mathrm{d}^3\mathbf{r}e^{-i\boldsymbol{K}\cdot\mathbf{r}}V(\mathbf{r})\,. \quad (7.3.33)$$

By spherical symmetry this integral just depends on the norm K of the vector $\mathbf{K}$. This is why we have a result that only depends on θ: while $\mathbf{K}$ is a vector that depends on both θ and ϕ, its magnitude only depends on θ. To do the integral think of $\boldsymbol{K}$ fixed and let Θ be

the angle with $\mathbf{r}$

$$f_k(\theta) = -\frac{m}{2\pi\hbar^2}\int_0^\infty 2\pi \mathrm{d}r\, r^2 \int_{-1}^{1} \mathrm{d}(\cos\Theta) e^{-iKr\cos\Theta} V(r)$$



$$= -\frac{m}{\hbar^2}\int_0^\infty \mathrm{d}r\, r^2 V(r)\frac{e^{-iKr}-e^{iKr}}{-iKr} = -\frac{m}{\hbar^2}\int_0^\infty \mathrm{d}r\, r^2 V(r)\left(\frac{2\sin(Kr)}{Kr}\right) \tag{7.3.34}$$

hence

$$\boxed{f_k(\theta) = -\frac{2m}{K\hbar^2}\int_0^\infty \mathrm{d}r\, rV(r)\sin(Kr)} \tag{7.3.35}$$

with $K = 2k\sin\frac{\theta}{2}$.

The Born approximation treats the potential as a perturbation of the free particle waves. This wave must therefore have kinetic energies larger than the potential. So most naturally, this is a good high-energy approximation.

Example: Yukawa potential Given

$$V(\mathbf{r}) = V(r) = \beta\frac{e^{-\mu r}}{r} \qquad \beta, \mu > 0 \tag{7.3.36}$$

from (7.3.35), one gets

$$f_k(\theta) = -\frac{2m\beta}{K\hbar^2}\int_0^\infty \mathrm{d}r\, e^{-\mu r}\sin(Kr) = -\frac{2m\beta}{\hbar^2(\mu^2+K^2)}\,. \tag{7.3.37}$$

We can give a graphical representation of the Born series. Two waves reach the desired point $\mathbf{r}$. The first is the direct incident wave. The second is a secondary wave originating at the scattering "material" at a point $\mathbf{r}'$. The amplitude of a secondary source at $\mathbf{r}'$ is given by the value of the incident wave times the *density* $U(\mathbf{r}')$ of scattering material at $\mathbf{r}'$.

In the second figure again an incident wave hits $\mathbf{r}$. The secondary wave now takes two steps: the incident wave hits scattering material at $\mathbf{r}''$ which then propagates and hits scattering material at $\mathbf{r}'$, from which it travels to point $\mathbf{r}$.

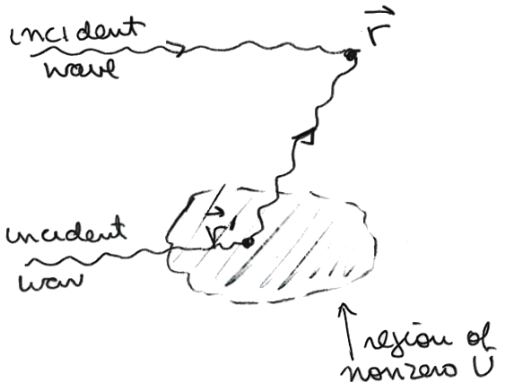


Figure 7.3: Pictorial view of Born approximation. Wave at $\mathbf{r}$ is the sum of the free incident wave at $\mathbf{r}$, plus an infinite number of waves coming from the secondary source at $\mathbf{r}'$, induced by the incident wave.

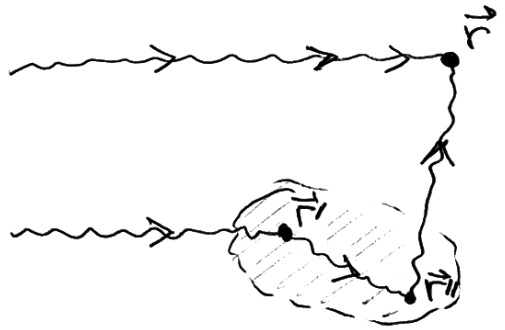


Figure 7.4: Pictorial view of second order Born term

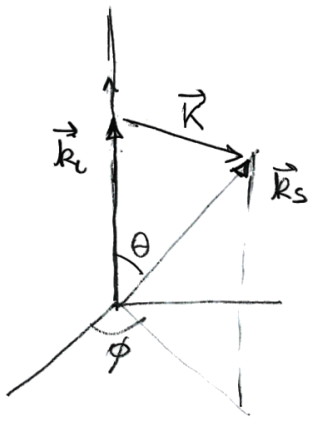


Figure 7.5: Given (θ, ϕ) and $\mathbf{k}$ ($\sim$ energy), $\boldsymbol{K}$ is determined.

Chapter 8

Identical Particles

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Two particles are *identical* if all their intrinsic properties (mass, spin, charge, magnetic moment, etc.) are the same and therefore no experiment can distinguish them. Of course, two identical particles can have different momentum, energy, angular momentum. For example all electrons are identical, all protons, all neutrons, all hydrogen atoms are identical (the possible excitation states viewed as energy, momentum, etc.)

8.1 Identical particles in Classical Mechanics

We can assign a labeling of the particles and follow through. Results are labeling independent.

As shown in Fig.8.2 we have two cases:

- Case 1: Assume we solve the dynamics and find

$$\begin{aligned} \mathbf{r}_1(t) &= \mathbf{r}(t) \qquad \text{with} \qquad \mathbf{r}(t_0) = \mathbf{r}_0 \\ \mathbf{r}_2(t) &= \mathbf{r}'(t) \qquad \text{with} \qquad \mathbf{r}'(t_0) = \mathbf{r}'_0 \end{aligned}$$

- Case 2: Since the particles are identical the Hamiltonian must make this clear

$$H(\mathbf{r}_1, \mathbf{p}_1; \mathbf{r}_2, \mathbf{p}_2) = H(\mathbf{r}_2, \mathbf{p}_2; \mathbf{r}_1, \mathbf{p}_1) \tag{8.1.1}$$

  This time, when we solve

$$\begin{aligned} \mathbf{r}_1(t) &= \mathbf{r}'(t) \qquad \text{with} \qquad \mathbf{r}'(t_0) = \mathbf{r}'_0 \\ \mathbf{r}_2(t) &= \mathbf{r}(t) \qquad \text{with} \qquad \mathbf{r}(t_0) = \mathbf{r}_0 \end{aligned}$$

The two descriptions are equivalent. We can follow the particles and the particle that started at $\{\mathbf{r}_0, \mathbf{p}_0\}$ will be at $\mathbf{r}(t)$, while the one that started at $\{\mathbf{r}'_0, \mathbf{p}'_0\}$ will be at $\mathbf{r}'(t)$.

In conclusion, we choose one labeling, just as if the particles were different. Follow through without regard to other possible labeling.

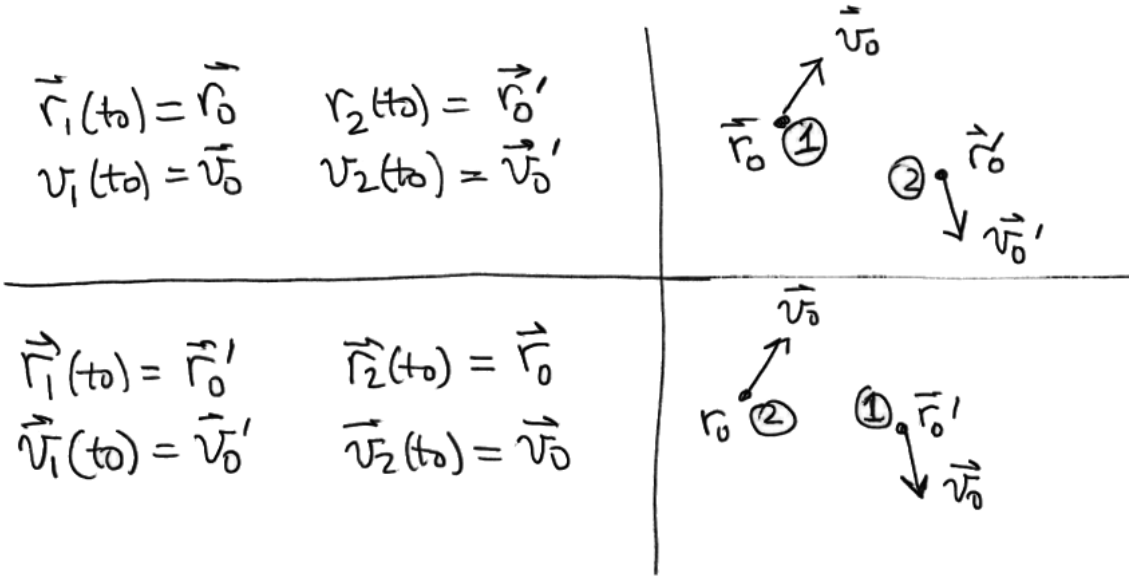


Figure 8.1: Example of two different ways of labeling the initial state

8.2 Identical particles in Quantum Mechanics

8.2.1 Exchange degeneracy

If we cannot follow particles once they overlap and/or collide, we can't know what alternative took place.
Question: How to write kets for the initial and final states?

Simpler case to see the complications Let there be two spin-1/2 particles. Consider only their spin[1], one is $|+\rangle$, the other $|-\rangle$. Recall tensor product $|v_i\rangle_{(1)} \otimes |v_j\rangle_{(2)}$ describing particle 1 in state v_i and particle 2 in state v_j. More briefly $|v_i\rangle_{(1)} \otimes |v_j\rangle_{(2)} \equiv |v_i\rangle \otimes |v_j\rangle$ with the understanding that the first ket is for particle 1 and the second for particle 2. What is the state of the two spin 1/2 particles?

$$|+\rangle_{(1)} \otimes |-\rangle_{(2)} \qquad \text{or} \qquad |-\rangle_{(1)} \otimes |+\rangle_{(2)} \tag{8.2.1}$$

A priori either one! This, despite the fact that in our conventions for inner products these two states are orthogonal! Can we declare these states to be physically equivalent and thus solve the ambiguity? No. If the two states above are equivalent we would have to admit that even the states

$$|\psi\rangle = \alpha|+\rangle \otimes |-\rangle + \beta|-\rangle \otimes |+\rangle \tag{8.2.2}$$

[1] in this approximation we could say that they are static and very close to each other, even on top of each other

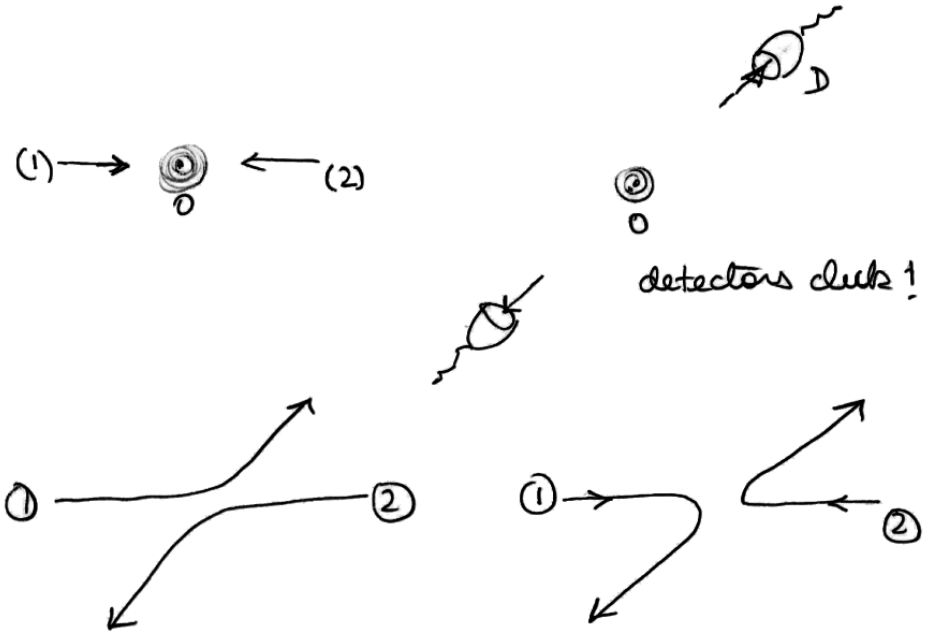


Figure 8.2: Example of two different processes involving identical particles. In principle, in quantum mechanics it is impossible to tell which one happened.

with $|\alpha|^2 + |\beta|^2 = 1$ for normalization, are equivalent. This ambiguity in the specification of a state of identical particles is called *exchange degeneracy*.
What is the probability to find these particles in the $|+,\chi\rangle \otimes |+,\chi\rangle$ state?
This states is

$$\begin{aligned} |\psi_0\rangle &= \frac{1}{\sqrt{2}}\Big(|+\rangle_{(1)} \ + \ |-\rangle_{(1)}\Big) \otimes \frac{1}{\sqrt{2}}\Big(|+\rangle_{(2)} \ + \ |-\rangle_{(2)}\Big) \\ &= \frac{1}{2}\Big(|+\rangle_{(1)} \otimes |+\rangle_{(2)} \ + \ |+\rangle_{(1)} \otimes |-\rangle_{(2)} \ + \ |-\rangle_{(1)} \otimes |+\rangle_{(2)} \ + \ |-\rangle_{(1)} \otimes |-\rangle_{(2)}\Big) \end{aligned} \tag{8.2.3}$$

the probability is

$$\Big|\langle\psi_0|\psi\rangle\Big|^2 = \Big|\frac{1}{2}(\alpha+\beta)\Big|^2 \tag{8.2.4}$$

thus a tremendous ambiguity because the chosen values of α, β matter!
Three particle degeneracy; 3 different eigenstates $|a\rangle, |b\rangle, |c\rangle$ give the following combinations

$$\begin{aligned} &|a\rangle_{(1)} \otimes |b\rangle_{(2)} \otimes |c\rangle_{(3)}\,, && |a\rangle_{(1)} \otimes |c\rangle_{(2)} \otimes |b\rangle_{(3)}\,, \\ &|b\rangle_{(1)} \otimes |c\rangle_{(2)} \otimes |a\rangle_{(3)}\,, && |b\rangle_{(1)} \otimes |a\rangle_{(2)} \otimes |c\rangle_{(3)}\,, \\ &|c\rangle_{(1)} \otimes |a\rangle_{(2)} \otimes |b\rangle_{(3)}\,, && |c\rangle_{(1)} \otimes |b\rangle_{(2)} \otimes |a\rangle_{(3)}\,. \end{aligned}$$

8.2.2 Permutation operators

Two particle systems

Consider the case when the vector space V relevant to the particles is the same for both particles, even though the particles may be *distinguishable*. Call the particles 1 and 2. Consider the state in which particle one is in state u_i and particle 2 in state u_j

$$|u_i\rangle_{(1)} \otimes |u_j\rangle_{(2)} \ \in V \otimes V \tag{8.2.5}$$

Since the particles are possibly distinguishable note that

$$|u_i\rangle_{(1)} \otimes |u_j\rangle_{(2)} \neq |u_j\rangle_{(1)} \otimes |u_i\rangle_{(2)} \,. \tag{8.2.6}$$

Define $\hat{P}_{21}$ the linear operator on $V \otimes V$ such that

$$\hat{P}_{21}\Big[|u_i\rangle_{(1)} \otimes |u_j\rangle_{(2)}\Big] \equiv |u_j\rangle_{(1)} \otimes |u_i\rangle_{(2)} \,. \tag{8.2.7}$$

note that

$$\hat{P}_{21}\hat{P}_{21} = \mathbb{1} \,, \tag{8.2.8}$$

i.e. $\hat{P}_{21}$ is its own inverse. Claim

$$\boxed{\hat{P}_{21}^\dagger = \hat{P}_{21} \,, \text{ Hermitian}} \tag{8.2.9}$$

Proof: First of all let's recall that for a generic operator $\hat{O}$, the adjoint of $\hat{O}$ is defined s.t.

$$\langle\alpha|\hat{O}^\dagger|\beta\rangle = \langle\beta|\hat{O}|\alpha\rangle \tag{8.2.10}$$

In our case, not writing the subscript labels,

$$\langle u_k| \otimes \langle u_\ell|\hat{P}_{21}|u_i\rangle \otimes |u_j\rangle = \langle u_k| \otimes \langle u_\ell|\Big(|u_j\rangle \otimes |u_i\rangle\Big) = \delta_{kj}\delta_{\ell i}$$
$$\langle u_k| \otimes \langle u_\ell|\hat{P}_{21}^\dagger|u_i\rangle \otimes |u_j\rangle = \Big(\langle u_i| \otimes \langle u_j|\hat{P}_{21}|u_k\rangle \otimes |u_\ell\rangle\Big)^* = \Big[\langle u_i| \otimes \langle u_j|\big(|u_\ell\rangle \otimes |u_k\rangle\big)\Big]^* = \Big[\delta_{i\ell}\delta_{jk}\Big]^* = \delta_{kj}\delta_{\ell i}$$

hence

$$\hat{P}_{21}^\dagger = \hat{P}_{21} \qquad \checkmark \,. \tag{8.2.11}$$

Because of (8.2.8) we also have that $\hat{P}_{21}$ is unitary:

$$\hat{P}_{21}^\dagger\hat{P}_{21} = \hat{P}_{21}\hat{P}_{21} = \mathbb{1} \,. \tag{8.2.12}$$

Given a generic state $|\psi\rangle$ it is not clear a priori what would it be its behaviour under the action of $\hat{P}_{21}$, hence to make our life easier we want to rewrite a generic state $|\psi\rangle$ in

terms of eigenstates of $\hat{P}_{21}$.
We can define two eigenstates of $\hat{P}_{21}$ with the following properties

$$\begin{aligned} \hat{P}_{21}|\psi_S\rangle &= |\psi_S\rangle && \text{Symmetric state} \\ \hat{P}_{21}|\psi_A\rangle &= -|\psi_A\rangle && \text{Antisymmetric state} \end{aligned}$$

and two operators $\hat{S}$ and $\hat{A}$

$$\hat{S} \equiv \frac{1}{2}(\mathbb{1} + \hat{P}_{21})\,, \qquad \hat{A} \equiv \frac{1}{2}(\mathbb{1} - \hat{P}_{21})\,. \tag{8.2.13}$$

Note that $\hat{S}$ and $\hat{A}$ are such that

$$\begin{aligned} \hat{P}_{21}\hat{S} &= \frac{1}{2}(\hat{P}_{21} + \hat{P}_{21}\hat{P}_{21}) = \frac{1}{2}(\hat{P}_{21} + \mathbb{1}) = \hat{S} \\ \hat{P}_{21}\hat{A} &= \frac{1}{2}(\hat{P}_{21} - \hat{P}_{21}\hat{P}_{21}) = \frac{1}{2}(\hat{P}_{21} - \mathbb{1}) = -\hat{A} \end{aligned}$$

Therefore, given a generic state $|\psi\rangle$ we have that

$$\begin{aligned} \hat{P}_{21}\hat{S}|\psi\rangle = \hat{S}|\psi\rangle \qquad &\Longrightarrow \qquad \hat{S}|\psi\rangle \text{ is symmetric} \\ \hat{P}_{21}\hat{A}|\psi\rangle = -\hat{A}|\psi\rangle \qquad &\Longrightarrow \qquad \hat{A}|\psi\rangle \text{ is anti-symmetric.} \end{aligned}$$

Because of this, the Hermitian operators $\hat{S}$ and $\hat{A}$ are called *symmetric/antisymmetric projectors*. From a mathematical point of view $\hat{S}$ and $\hat{A}$ are orthogonal projectors[2] and satisfy

$$\hat{S}^2 = \hat{S}\,, \qquad \hat{A}^2 = \hat{A}\,, \qquad \hat{S} + \hat{A} = \mathbb{1}\,, \qquad \hat{S}\hat{A} = \hat{A}\hat{S} = 0\,. \tag{8.2.15}$$

Action on operators Let $B(n)$ be an operator acting on the n-th vector space, i.e.

$$\begin{aligned} B(1)|u_i\rangle_{(1)} \otimes |u_j\rangle_{(2)} &= \Big(B|u_i\rangle\Big)_{(1)} \otimes |u_j\rangle_{(2)} \\ B(2)|u_i\rangle_{(1)} \otimes |u_j\rangle_{(2)} &= |u_i\rangle_{(1)} \otimes \Big(B|u_j\rangle\Big)_{(2)} \end{aligned}$$

then the action of $\hat{P}_{21}$ on $B(1)$ is

$$\begin{aligned} \hat{P}_{21}B(1)\hat{P}_{21}^\dagger|u_i\rangle_{(1)} \otimes |u_j\rangle_{(2)} &= \hat{P}_{21}B(1)|u_j\rangle_{(1)} \otimes |u_i\rangle_{(2)} \\ &= \hat{P}_{21}\Big(B|u_j\rangle\Big)_{(1)} \otimes |u_i\rangle_{(2)} = |u_i\rangle_{(1)} \otimes \Big(B|u_j\rangle\Big)_{(2)} = B(2)|u_i\rangle \otimes |u_j\rangle \end{aligned} \tag{8.2.16}$$

[2] A projector $P : V \to U \subset V$ is *orthogonal* if $V = \ker P \oplus \text{range } P$, with $\ker P \perp \text{range } P$. Take $v \in V$, then

$$v = \underbrace{Pv}_{\text{range}P} + \underbrace{v - Pv}_{\ker P} = u + w \tag{8.2.14}$$

where $w \in \ker P$, $u = Pv \in \text{range}P$, then $\ker P \perp \text{range}P$ because

$$\langle w, u\rangle = \langle w, Pv\rangle = \langle P^\dagger w, v\rangle = \langle Pw, v\rangle = \langle 0, v\rangle = 0$$

hence

$$\boxed{\hat{P}_{21}B(1)\hat{P}_{21}^{\dagger} = B(2)} \tag{8.2.17}$$

Similarly we have

$$\hat{P}_{21}B(2)\hat{P}_{21}^{\dagger} = B(1) \tag{8.2.18}$$

and if we consider a generic operator $\hat{\Theta}(1,2)$, then

$$\boxed{\hat{P}_{21}\hat{\Theta}(1,2)\hat{P}_{21}^{\dagger} = \hat{\Theta}(2,1)}\,. \tag{8.2.19}$$

Note that if $\hat{\Theta}(1,2) = \hat{\Theta}(2,1)$ we say $\hat{\Theta}(1,2)$ is *symmetric*. If an operator is symmetric then

$$\begin{aligned} 0 &= \hat{P}_{21}\hat{\Theta}(1,2)\hat{P}_{21}^{\dagger} - \hat{\Theta}(1,2) \\ 0 &= \hat{P}_{21}\hat{\Theta}(1,2) - \hat{\Theta}(1,2)\hat{P}_{21} \\ 0 &= [\hat{P}_{21}, \hat{\Theta}(1,2)] \end{aligned} \tag{8.2.20}$$

$$[\hat{P}_{21}, \hat{\Theta}(1,2)] = 0 \iff \hat{\Theta} \text{ is symmetric}\,. \tag{8.2.21}$$

N particle systems

In a N particle system we can define $N!$ permutation operators $\hat{P}_{i_1,\ldots,i_N}$, with $\hat{P}_{12\ldots N}$ being the identity. For a 3-particle system, for example, the operator P_{npq} acting on a state has the effect of

$$\hat{P}_{npq} \qquad \text{means} \qquad \begin{aligned} n &\to 1 \qquad & n-\text{th state moved to position 1} \\ p &\to 2 \qquad & p-\text{th state moved to position 2} \\ q &\to 3 \qquad & q-\text{th state moved to position 3} \end{aligned}$$

e.g.

$$\hat{P}_{231}|u_i\rangle_{(1)} \otimes |u_j\rangle_{(2)} \otimes |u_k\rangle_{(3)} = |u_j\rangle_{(1)} \otimes |u_k\rangle_{(2)} \otimes |u_i\rangle_{(3)} \tag{8.2.22}$$

You should check that its inverse is $\hat{P}_{312}$, so that

$$\hat{P}_{231}\hat{P}_{312} = \mathbb{1}\,. \tag{8.2.23}$$

More formally we can define a *permutation* of N numbers by the function α that maps the standard ordered integers $1, \ldots, N$ into some arbitrary ordering of them

$$\alpha : [1, 2, \ldots, N] \to [\alpha(1),\, \alpha(2),\, \ldots,\, \alpha(N)] \tag{8.2.24}$$

and associate it with a permutation operator

$$\hat{P}_{\alpha} \equiv \hat{P}_{\alpha(1),\,\alpha(2),\,\ldots,\,\alpha(N)} \tag{8.2.25}$$

$$\hat{P}_{\alpha}|u_1\rangle_{(1)} \otimes \cdots \otimes |u_N\rangle_{(N)} = |u_{\alpha(1)}\rangle_{(1)} \otimes \cdots \otimes |u_{\alpha(N)}\rangle_{(N)} \tag{8.2.26}$$

For example

$$\hat{P}_{3142}|u_1\rangle_{(1)} \otimes |u_2\rangle_{(2)} \otimes |u_3\rangle_{(3)} \otimes |u_4\rangle_{(4)} = |u_3\rangle_{(1)} \otimes |u_1\rangle_{(2)} \otimes |u_4\rangle_{(3)} \otimes |u_2\rangle_{(4)} \tag{8.2.27}$$

or

$$\hat{P}_{3142}|a\rangle_{(1)} \otimes |b\rangle_{(2)} \otimes |c\rangle_{(3)} \otimes |d\rangle_{(4)} = |c\rangle_{(1)} \otimes |a\rangle_{(2)} \otimes |d\rangle_{(3)} \otimes |b\rangle_{(4)} \tag{8.2.28}$$

The set of all permutations of N objects forms the *symmetric group* S_N and it has $N!$ elements. For S_3 we have 6 elements or the 6 permutation operators:

$$\underbrace{\hat{P}_{123}}_{\mathbb{1}} \overset{\text{cyclic}}{\to} \hat{P}_{312} \overset{\text{cyclic}}{\to} \hat{P}_{231}\,, \quad \underbrace{\hat{P}_{132} \overset{\text{cyclic}}{\to} \hat{P}_{213} \overset{\text{cyclic}}{\to} \hat{P}_{321}}_{\substack{\text{these are } \textit{transpositions},\\ \text{a permutation in which only}\\ \text{2 particles are exchanged}\\ \text{without affecting the rest}}}$$

$\hat{P}_{132}$ is a transposition in which the states of the second and third particles are exchanged while the first particle is left unchanged. For transpositions we sometimes use the notation where we just indicate the two labels that are being transposed. Those two labels could be written in any order without risk of confusion, but we will use ascending order:

$$\begin{aligned} (12) &\equiv P_{213} \\ (13) &\equiv P_{321} \\ (23) &\equiv P_{132} \end{aligned} \tag{8.2.29}$$

While all permutations that are transpositions are Hermitian (see the proof for $\hat{P}_{21}$ that easily generalizes), general permutations are not Hermitian. It is intuitively clear that any permutation can be written as product of transpositions: any set of integers can be reordered into any arbitrary position by transpositions (in fact by using transpositions of consecutive labels). The decomposition of a permutation into a product of transpositions is not unique, but it is unique (mod 2). Hence we have that every permutation is either *even* or *odd*. A permutation is said to be even if it is the product of an even number of transpositions, and it is said to be odd if it is the product of an odd number of transpositions.

Since transposition operators are and unitary any permutation is a unitary operator. All transpositions are also Hermitian, but an arbitrary product of them is not hermitian because the transpositions do not necessarily commute.

In fact, the Hermitian conjugate of a permutation is its inverse, which is a permutation of the same parity. This is clear from writing $\hat{P}_\alpha$ as a product of transpositions P_{t_i}:

$$\begin{aligned} \hat{P}_\alpha &= \hat{P}_{t_1}\hat{P}_{t_2}\ldots\hat{P}_{t_k} \\ \hat{P}_\alpha^\dagger &= \hat{P}_{t_k}^\dagger\ldots\hat{P}_{t_2}^\dagger\hat{P}_{t_1}^\dagger = \hat{P}_{t_k}\ldots\hat{P}_{t_2}\hat{P}_{t_1} \end{aligned} \tag{8.2.30}$$

and therefore

$$\implies \hat{P}_\alpha\hat{P}_\alpha^\dagger = \mathbb{1} \tag{8.2.31}$$

Theorem 8.2.1. *The number of even permutations is the same as the number of odd permutations*

Proof. Consider the map that multiplies any permutation by (12) from the left (12) : $P_{\text{even}} \to P_{\text{odd}}$ so that if $\sigma \in P_{\text{even}}$ then $(12)\sigma \in P_{\text{odd}}$. This map is one to one

$$(12)\sigma = (12)\sigma' \implies \sigma = \sigma' \,, \tag{8.2.32}$$

by multiplying from the left by (12), which is the inverse of (12). This map is also surjective or onto:for any $\beta \in P_{\text{odd}}$, we have $\beta = (12)\underbrace{(12)\beta}_{\in P_{\text{even}}}$. □

$A\backslash B$	$\hat{P}_{312}$	$\hat{P}_{231}$	(23)	(12)	(13)
$\hat{P}_{312}$	$\hat{P}_{231}$	$\mathbb{1}$	(12)	(13)	(23)
$\hat{P}_{231}$	$\mathbb{1}$	$\hat{P}_{312}$	(13)	(23)	(12)
(23)	(13)	(12)	$\mathbb{1}$	$\hat{P}_{231}$	$\hat{P}_{312}$
(12)	(23)	(13)	$\hat{P}_{312}$	$\mathbb{1}$	$\hat{P}_{231}$
(13)	(12)	(23)	$\hat{P}_{231}$	$\hat{P}_{312}$	$\mathbb{1}$

Table 8.1: $A \cdot B$ matrix for S_3.

Complete symmetrizer and antisymmetrizer

Permutation operators do not commute, so we can't find complete basis of states that are eigenstates of all permutation operators. It is possible, however, to find some states that are simultaneous eigenvectors of all permutation operators.

Consider N particles, each with the same vector space. Let $\hat{P}_\alpha$ be an arbitrary permutation, then

$$\begin{aligned} \text{Symmetric state } |\psi_S\rangle \ : \quad & \hat{P}_\alpha|\psi_S\rangle = |\psi_S\rangle \quad \forall\alpha \\ \text{Antisymmetric state } |\psi_A\rangle \ : \quad & \hat{P}_\alpha|\psi_A\rangle = \epsilon_\alpha|\psi_A\rangle \end{aligned}$$

where

$$\epsilon_\alpha = \begin{cases} +1 & \text{if } \hat{P}_\alpha \text{ is an even permutation} \\ -1 & \text{if } \hat{P}_\alpha \text{ is an odd permutation} \end{cases} \tag{8.2.33}$$

In the total Hilbert space $V^{\otimes N} \equiv \underbrace{V \otimes \cdots \otimes V}_{N}$, we can identify a subspace $\text{Sym}^N V \subset V^{\otimes N}$ of symmetric states and a subspace $\text{Anti}^N V \subset V^{\otimes N}$ of antisymmetric states. Can we construct projectors into such subspaces?

Yes!

$$\hat{S} \equiv \frac{1}{N!}\sum_\alpha \hat{P}_\alpha \qquad \text{and} \qquad \hat{A} \equiv \frac{1}{N!}\sum_\alpha \epsilon_\alpha \hat{P}_\alpha \tag{8.2.34}$$

where we sum over all $N!$ permutations. $\hat{S}$ is called the *symmetrizer* and $\hat{A}$ is called the *antisymmetrizer*.

$$\text{Claim:} \qquad \hat{S} = \hat{S}^\dagger \qquad \hat{A} = \hat{A}^\dagger \tag{8.2.35}$$

Hermitian conjugation of $\hat{P}_\alpha$ gives $\hat{P}_\alpha^{-1}$ which is even if $\hat{P}_\alpha$ is even and odd if $\hat{P}_\alpha$ is odd. Thus Hermitian conjugation just rearranges the sums, leaving them invariant.
Moreover

$$\hat{P}_{\alpha_0}\hat{S} = \hat{S}\hat{P}_{\alpha_0} = \hat{S} \tag{8.2.36}$$

$$\hat{P}_{\alpha_0}\hat{A} = \hat{A}\hat{P}_{\alpha_0} = \epsilon_{\alpha_0}\hat{A} \tag{8.2.37}$$

Proof. Note that $\hat{P}_{\alpha_0}$ acting on the list of permutations simply rearranges the list, given two permutations $P_{\gamma_1} \neq P_{\gamma_2}$ then $\hat{P}_{\alpha_0}P_{\gamma_1} \neq \hat{P}_{\alpha_0}P_{\gamma_2}$, hence

$$\hat{P}_{\alpha_0}\hat{S} = \hat{P}_{\alpha_0}\frac{1}{N!}\sum_\alpha \hat{P}_\alpha = \frac{1}{N!}\sum_\alpha \hat{P}_{\alpha_0}\hat{P}_\alpha = \frac{1}{N!}\sum_\beta \hat{P}_\beta = \hat{S} \qquad \checkmark \tag{8.2.38}$$

analogously

$$\begin{aligned}\hat{P}_{\alpha_0}\hat{A} &= \hat{P}_{\alpha_0}\frac{1}{N!}\sum_\alpha \epsilon_\alpha \hat{P}_\alpha = \frac{1}{N!}\sum_\alpha \epsilon_\alpha \hat{P}_{\alpha_0}\hat{P}_\alpha = \frac{1}{N!}\sum_\alpha \epsilon_\alpha \underbrace{\epsilon_{\alpha_0}\epsilon_{\alpha_0}}_{=1}\hat{P}_{\alpha_0}\hat{P}_\alpha \\ &= \frac{\epsilon_{\alpha_0}}{N!}\sum_\alpha \epsilon_\alpha\epsilon_{\alpha_0}\hat{P}_{\alpha_0}\hat{P}_\alpha = \frac{\epsilon_{\alpha_0}}{N!}\sum_\beta \epsilon_\beta \hat{P}_\beta = \epsilon_{\alpha_0}\hat{A} \qquad \checkmark\end{aligned} \tag{8.2.39}$$

□

Finally they are projectors

$$\boxed{\hat{S}^2 = \hat{S}\,, \qquad \hat{A}^2 = \hat{A}\,, \qquad \hat{S}\hat{A} = \hat{A}\hat{S} = 0} \tag{8.2.40}$$

$$\hat{S}^2 = \frac{1}{N!}\sum_\alpha \hat{P}_\alpha\hat{S} = \frac{1}{N!}\sum_\alpha \hat{S} = \frac{1}{N!}N!\,\hat{S} = \hat{S} \qquad \checkmark \tag{8.2.41}$$

$$\hat{A}^2 = \frac{1}{N!}\sum_\alpha \epsilon_\alpha\hat{P}_\alpha\hat{A} = \frac{1}{N!}\sum_\alpha \epsilon_\alpha\epsilon_\alpha\hat{A} = \frac{1}{N!}\sum_\alpha \hat{A} = \frac{1}{N!}N!\,\hat{A} = \hat{A} \qquad \checkmark \tag{8.2.42}$$

$$\hat{A}\hat{S} = \frac{1}{N!}\sum_\alpha \epsilon_\alpha\hat{P}_\alpha\hat{S} = \frac{1}{N!}\sum_\alpha \epsilon_\alpha\hat{S} = \frac{\hat{S}}{N!}\sum_\alpha \epsilon_\alpha = 0 \qquad \checkmark \tag{8.2.43}$$

Since, as explained before there are equal numbers of even and odd permutations, i.e. $\sum_\alpha \epsilon_\alpha = 0$.
Note that

$$\hat{S}|\psi\rangle \in \mathrm{Sym}^N V \quad \text{since} \quad \hat{P}_\alpha\hat{S}|\psi\rangle = \hat{S}|\psi\rangle \;\forall\,\alpha \tag{8.2.44}$$

and analogously

$$\hat{A}|\psi\rangle \in \mathrm{Anti}^N V \quad \text{since} \quad \hat{P}_\alpha\hat{A}|\psi\rangle = \epsilon_\alpha\hat{A}|\psi\rangle \;\forall\,\alpha \tag{8.2.45}$$

Hence, they are, as claimed, projectors into the symmetric and antisymmetric subspaces:

$$\hat{S} : V^{\otimes N} \to \mathrm{Sym}^N V\,, \qquad \hat{A} : V^{\otimes N} \to \mathrm{Anti}^N V \tag{8.2.46}$$

Example: $N = 3$ For S_3 we have 6 elements or the 6 permutation operators:

$$\hat{P}_{123} = \mathbf{1}\,,\ \hat{P}_{312}\,,\ \hat{P}_{231}\,,\ \hat{P}_{132}\,,\ \hat{P}_{213}\,,\ \hat{P}_{321}$$

In this case the symmetrizer and antisymmetrizer operators $\hat{S}$ and $\hat{A}$ are

$$\hat{S} = \tfrac{1}{6}(\mathbf{1} + \hat{P}_{312} + \hat{P}_{231} + \hat{P}_{132} + \hat{P}_{213} + \hat{P}_{321}) \tag{8.2.47}$$

$$\hat{A} = \tfrac{1}{6}(\mathbf{1} + \hat{P}_{312} + \hat{P}_{231} - \hat{P}_{132} - \hat{P}_{213} - \hat{P}_{321}) \tag{8.2.48}$$

Note that

$$\hat{S} + \hat{A} = \tfrac{1}{3}(\mathbf{1} + \hat{P}_{312} + \hat{P}_{231}) \neq \mathbb{1} = \hat{P}_{123} \tag{8.2.49}$$

This is a manifestation of the fact that in general for $N > 2$, we have

$$\mathrm{Sym}^N V \oplus \mathrm{Anti}^N V \subset V^{\otimes N} \tag{8.2.50}$$

i.e. in principle, the N-particle Hilbert space is not spanned by purely symmetric or antisymmetric states.
We define $\Theta(1, 2, \ldots, N)$ to be a *completly symmetric observable* if

$$[\Theta(1, 2, \ldots, N), \hat{P}_\alpha] = 0 \quad \forall\alpha \tag{8.2.51}$$

8.3 The symmetrization postulate

In a system with N identical particles the states that are physically realized are not arbitrary states in $V^{\otimes N}$, but rather they are totally symmetric (*i.e.* belong to $\mathrm{Sym}^N V$), in which case the particles are said to be *bosons*, or they are totally antisymmetric (*i.e.* belong to $\mathrm{Anti}^N V$) in which case they are said to be *fermions*.

Comments:

1. The above is a statement of fact in 3D. Alternative possibilities can happen in worlds with 2 spatial dimensions (anyons)

2. The postulate describes the statistical behaviour of bosons and of fermions

3. Spin-statistics theorem from Quantum Field Theory shows that bosons are particles of integer spins (0, 1, 2, ...) while fermions are particles of half-integer spin (1/2, 3/2 , ...)

4. The symmetrization postulate for elementary particles lead to a definite character, as bosons or fermions, for composite particles, which in turn obey the symmetrization

postulate. Take for example two hydrogen atoms

p = proton is a fermion (spin 1/2)
e = electron is a fermion (")

The system is made by 4 particles and its total wavefunction is $\Psi(p_1, e_1; p_2, e_2)$. Since the two electrons are identical particles of spin 1/2, the wavefunction must be anti-symmetric under the exchange $e_1 \leftrightarrow e_2$

$$\Psi(p_1, e_2; p_2, e_1) = -\Psi(p_1, e_1; p_2, e_2)\,. \tag{8.3.1}$$

Exactly the same argument applies to the protons,

$$\Psi(p_2, e_1; p_1, e_2) = -\Psi(p_1, e_1; p_2, e_2)\,. \tag{8.3.2}$$

Therefore under the simultaneous exchange

$$\Psi(p_2, e_2; p_1, e_1) = +\Psi(p_1, e_1; p_2, e_2)\,. \tag{8.3.3}$$

The exchange in (8.3.3) corresponds to $p_1 \leftrightarrow p_2$ *and* $e_1 \leftrightarrow e_2$, an exchange of the two hydrogen atoms! Since the wavefunction is symmetric under this exchange, (8.3.3) shows that the hydrogen atom is a boson!

5. The symmetrization postulate solves the exchange degeneracy problem.

   Say $|u\rangle \in V^{\otimes N}$ represents mathematically a state. Let $V_{|u\rangle} \equiv \text{span}\left\{\hat{P}_\alpha|u\rangle\,, \forall\alpha\right\}$. Depending on $|u\rangle$ the dimension of $V_{|u\rangle}$ can go from 1 to $N!$. This dimensionality, if different from one, is the degeneracy due to exchange.

   The exchange degeneracy problem (*i.e.* the ambiguity in finding a representative for the physical state in $V_{|u\rangle}$) is solved by the symmetrization postulate by showing that $V_{|u\rangle}$ contains, up to scale, a single ket of $\text{Sym}^N V$ and a single ket of $\text{Anti}^N V$.

Proof. Suppose we have two states $|\psi\rangle$, $|\psi'\rangle \in V_{|u\rangle}$ that both happen to be symmetric: $|\psi\rangle$, $|\psi'\rangle \in \text{Sym}^N V$. We can write them as

$$|\psi\rangle = \sum_\alpha c_\alpha P_\alpha|u\rangle \quad \text{and} \quad |\psi'\rangle = \sum_\alpha c'_\alpha P_\alpha|u\rangle \tag{8.3.4}$$

with c_α, c'_α some coefficients. Then, since $|\psi\rangle \in \mathrm{Sym}^N V$

$$|\psi\rangle = \hat{S}|\psi\rangle = \hat{S}\sum_\alpha c_\alpha P_\alpha |u\rangle = \sum_\alpha c_\alpha \hat{S} P_\alpha |u\rangle = \sum_\alpha c_\alpha \hat{S}|u\rangle = \hat{S}|u\rangle \sum_\alpha c_\alpha \,. \tag{8.3.5}$$

Analogously

$$|\psi'\rangle = \hat{S}|u\rangle \sum_\alpha c'_\alpha \,. \tag{8.3.6}$$

Hence $|\psi\rangle \propto |\psi'\rangle$, the states are the same up to scale. □

6. Building antisymmetric states.

Constructing the three-particle state $\hat{A}|u\rangle$ with $|u\rangle \in V^{\otimes 3}$ given by

$$|u\rangle = |\varphi\rangle_{(1)} \otimes |\chi\rangle_{(2)} \otimes |\omega\rangle_{(3)} \tag{8.3.7}$$

The claim is that the antisymmetric state is constructed by a determinant:

$$\hat{A}|u\rangle = \tfrac{1}{3!}\sum_\alpha \epsilon_\alpha \hat{P}_\alpha |\varphi\rangle_{(1)} \otimes |\chi\rangle_{(2)} \otimes |\omega\rangle_{(3)} = \tfrac{1}{3!}\begin{vmatrix} |\varphi\rangle_{(1)} & |\varphi\rangle_{(2)} & |\varphi\rangle_{(3)} \\ |\chi\rangle_{(1)} & |\chi\rangle_{(2)} & |\chi\rangle_{(3)} \\ |\omega\rangle_{(1)} & |\omega\rangle_{(2)} & |\omega\rangle_{(3)} \end{vmatrix} \tag{8.3.8}$$

When writing the products in the determinant one must reorder each term to have the standard order $|\cdot\rangle_{(1)} \otimes |\cdot\rangle_{(2)} \otimes |\cdot\rangle_{(3)}$. You can confirm you get the right answer. Now do it generally. Recall the formula for the determinant of a matrix

$$\det \hat{B} = \sum_\alpha \epsilon_\alpha B_{\alpha(1),1} B_{\alpha(2),2} \ldots B_{\alpha(N),N} \tag{8.3.9}$$

Let $|\omega\rangle$ be a generic state $\in V^{\otimes N}$

$$|\omega\rangle = |\omega_1\rangle_{(1)} |\omega_2\rangle_{(2)} \ldots |\omega_N\rangle_{(N)} \tag{8.3.10}$$

then

$$\hat{P}_\alpha |\omega\rangle = |\omega_{\alpha(1)}\rangle_{(1)} |\omega_{\alpha(2)}\rangle_{(2)} \ldots |\omega_{\alpha(N)}\rangle_{(N)} \tag{8.3.11}$$

so that

$$\hat{A}|\omega\rangle = \frac{1}{N!}\sum_\alpha \epsilon_\alpha \hat{P}_\alpha |\omega\rangle = \frac{1}{N!}\sum_\alpha \epsilon_\alpha |\omega_{\alpha(1)}\rangle_{(1)} |\omega_{\alpha(2)}\rangle_{(2)} \ldots |\omega_{\alpha(N)}\rangle_{(N)} \,. \tag{8.3.12}$$

If we define a matrix

$$\omega_{ij} \equiv |\omega_i\rangle_{(j)} \tag{8.3.13}$$

then

$$\hat{A}|\omega\rangle = \frac{1}{N!}\sum_\alpha \epsilon_\alpha \omega_{\alpha(1),1} \omega_{\alpha(2),2} \ldots \omega_{\alpha(N),N} = \frac{1}{N!}\det(\omega) \tag{8.3.14}$$

i.e.

$$\hat{A}|\omega\rangle = \frac{1}{N!}\begin{vmatrix} |\omega_1\rangle_{(1)} & |\omega_1\rangle_{(2)} & \dots & |\omega_1\rangle_{(N)} \\ |\omega_2\rangle_{(1)} & |\omega_2\rangle_{(2)} & \dots & |\omega_2\rangle_{(N)} \\ \vdots & & & \vdots \\ |\omega_N\rangle_{(1)} & \dots & \dots & |\omega_N\rangle_{(N)} \end{vmatrix} \tag{8.3.15}$$

8.4 Occupation numbers

Consider a system of N identical particle. Basis states in $V^{\otimes N}$ take the form

$$|u_i\rangle_{(1)} \otimes \dots |u_p\rangle_{(N)} \tag{8.4.1}$$

where the one-particle states form an orthonormal basis of V:

$$V = \text{span}\{|u_1\rangle, |u_2\rangle, \dots\} \tag{8.4.2}$$

By applying $\hat{S}$ or $\hat{A}$ to the full set of states in $V^{\otimes N}$ we obtain all physical states in $\text{Sym}^N V$ and $\text{Anti}^N V$. But many different states in $V^{\otimes N}$ can give rise to the *same* state in $\text{Sym}^N V$ and $\text{Anti}^N V$ after the application of the projectors.

To distinguish basis states in $V^{\otimes N}$ that after application of $\hat{S}$ or $\hat{A}$ are linearly independent, define the *occupation number*. We assign a set of occupation numbers to a basis state $|\cdot\rangle \otimes \cdots \otimes |\cdot\rangle$. An occupation number is an integer $n_i \geq 0$ associated with each vector in V:

$$\underset{n_1}{|u_1\rangle}, \ \underset{n_2}{|u_2\rangle}, \ \dots, \ \underset{n_k}{|u_k\rangle}, \ \dots \tag{8.4.3}$$

We define n_k to be the number of times that $|u_k\rangle$ appears in the chosen basis state $|\cdot\rangle \otimes \cdots \otimes |\cdot\rangle$. Thus, by inspection of the state $|\cdot\rangle \otimes \cdots \otimes |\cdot\rangle$ we can read all the occupation numbers $n_1, n_2, \cdots$. It should be clear that the action of a permutation operator on a basis state in $V^{\otimes N}$ will not change the occupation numbers.

Two basis states in $V^{\otimes N}$ with the same occupation numbers can be mapped into each other by a permutation operator; they lead to the same state in $\text{Sym}^N V$ and to the same state (up to a sign) in $\text{Anti}^N V$. Two basis states in $V^{\otimes N}$ with different occupation numbers cannot be mapped into each other by a permutation operator. They must lead to different states in $\text{Sym}^N V$ and to different states in $\text{Anti}^N V$, unless they give zero.

Given the occupation numbers of a basis state, we denote the associated basis state in $\text{Sym}^N V$ as follows

$$|n_1, n_2, \dots\rangle_S \qquad\qquad n_i \geq 0 \tag{8.4.4}$$

Explicitly

$$|n_1,\, n_2,\, \ldots\rangle_S \;\equiv\; c_S\, \hat{S}\, \underbrace{|u_1\rangle \ldots |u_1\rangle}_{n_1 \text{ times}} \otimes \underbrace{|u_2\rangle \ldots |u_2\rangle}_{n_2 \text{ times}} \otimes \ldots \tag{8.4.5}$$

where c_S is a constant that is used to give the state unit normalization. More briefly we write

$$|n_1,\, n_2,\, \ldots\rangle_S \;\equiv\; c_S\, \hat{S}\, |u_1\rangle^{\otimes n_1} \otimes\; |u_2\rangle^{\otimes n_2} \otimes \ldots \tag{8.4.6}$$

where $|u_i\rangle^{\otimes n_i}$ is equal to 1 when $n_i = 0$ These states form an orthonormal basis in $\mathrm{Sym}^N V$:

$${}_S\langle n_1',\, n_2',\, \ldots | n_1,\, n_2,\, \ldots\rangle_S = \delta_{n_1,n_1'}\delta_{n_2,n_2'} \ldots \tag{8.4.7}$$

The space $\mathrm{Sym}^N V$ relevant to identical bosons is spanned by all the states

$$|n_1,\, n_2,\, \ldots\rangle \qquad \text{with } \sum_k n_k = N \tag{8.4.8}$$

The space $\mathrm{Anti}^N V$ relevant to identical fermions is spanned by all the states

$$|n_1,\, n_2,\, \ldots\rangle_A \qquad \text{with } \sum_k n_k = N \;\text{ and }\; n_k \in \{0,1\}\,, \tag{8.4.9}$$

since occupation numbers cannot be greater than one (any state with an occupation number two or larger is killed by $\hat{A}$). We have

$$|n_1,\, n_2,\, \ldots\rangle_A \;\equiv\; c_A\, \hat{A}\, |u_1\rangle^{\otimes n_1} \otimes\; |u_2\rangle^{\otimes n_2} \;\otimes \ldots \tag{8.4.10}$$

where c_A is a constant that is used to give the state unit normalization. These states form an orthonormal basis in $\mathrm{Anti}^N V$.

8.5 Particles that live in $V \otimes W$

A particle may have space degrees of freedom, described by a vector space V and spin degree of freedom associated with W. Suppose we have a state than of 2 such particles described in $(V \otimes W)^{\otimes 2}$ for example

$$|\psi\rangle = |v_i\rangle_{(1)} \otimes |w_i\rangle_{(1)} \otimes |v_j\rangle_{(2)} \otimes |w_j\rangle_{(2)} + \ldots \tag{8.5.1}$$

This ψ should belongs either to $\mathrm{Sym}^2(V \otimes W)$ or to $\mathrm{Anti}^2(V \otimes W)$. The permutation operator here that exchange particles 1 and 2 is

$$\hat{P}_{3412}|\psi\rangle = \hat{P}_{3412}\Big(|v_i\rangle_{(1)} \otimes |w_i\rangle_{(1)} \otimes |v_j\rangle_{(2)} \otimes |w_j\rangle_{(2)}\Big) = |v_j\rangle_{(1)} \otimes |w_j\rangle_{(1)} \otimes |v_i\rangle_{(2)} \otimes |w_i\rangle_{(2)} \tag{8.5.2}$$

Wanto to express this in terms of $\mathrm{Sym}^2 V$, $\mathrm{Anti}^2 V$, $\mathrm{Sym}^2 W$, $\mathrm{Anti}^2 W$.
Why? Because it is possible: for any state

$$\ldots \overset{W}{|a\rangle} \ldots \overset{W}{|b\rangle} = \frac{1}{2}\underbrace{\Big(\ldots |a\rangle \ldots |b\rangle + \ldots |b\rangle \ldots |a\rangle\Big)}_{\in \mathrm{Sym}^2 W} + \frac{1}{2}\underbrace{\Big(\ldots |a\rangle \ldots |b\rangle - \ldots |b\rangle \ldots |a\rangle\Big)}_{\in \mathrm{Anti}^2 W} \tag{8.5.3}$$

Thus we can assume we work with simultaneous eigenstates of $\hat{P}_{3214}$, which exchanges the V states, and of $\hat{P}_{1432}$, which exchanges the W states. Note that

$$\hat{P}_{3412} = \hat{P}_{3214}\hat{P}_{1432} \tag{8.5.4}$$

where the order is not important since $[\hat{P}_{3214}, \hat{P}_{1432}] = 0$.
The eigenvalues are

$\hat{P}_{3214}$	$\hat{P}_{1432}$	$\hat{P}_{3412}$
1	1	1
-1	-1	1
1	-1	-1
-1	1	-1

This means that

$$\mathrm{Sym}^2(V \otimes W) \simeq \left(\mathrm{Sym}^2 V \otimes \mathrm{Sym}^2 W\right) \oplus \left(\mathrm{Anti}^2 V \otimes \mathrm{Anti}^2 W\right) \tag{8.5.5}$$

$$\mathrm{Anti}^2(V \otimes W) \simeq \left(\mathrm{Sym}^2 V \otimes \mathrm{Anti}^2 W\right) \oplus \left(\mathrm{Anti}^2 V \otimes \mathrm{Sym}^2 W\right) \tag{8.5.6}$$

where with $\simeq$ we indicate

$$|v_i\rangle_{(1)} \otimes |w_i\rangle_{(1)} \otimes |v_j\rangle_{(2)} \otimes |w_j\rangle_{(2)} \simeq |v_i\rangle_{(1)} \otimes |v_j\rangle_{(1)} \otimes |w_i\rangle_{(2)} \otimes |w_j\rangle_{(2)} \,. \tag{8.5.7}$$

The generalization to 2 particle belonging to $(U \otimes V \otimes W)$ is simple, for 3 or more particle is more complicated.

Example. Two electrons with spin wavefunction

$$\Psi(\mathbf{x_1}, m_1; \mathbf{x_1}, m_2) = \phi(x_1, x_2) \cdot \chi(m_1, m_2) \qquad \hat{S}_z = m\hbar \tag{8.5.8}$$

χ can be some normalized state in the space spanned by the triplet and the singlet. The probability $\mathrm{d}P$ to find one electron in $\mathrm{d}^3\mathbf{x_1}$ around $\mathbf{x_1}$ and in $\mathrm{d}^3\mathbf{x_2}$ around $\mathbf{x_2}$ is

$$dP = |\phi(\mathbf{x_1}, \mathbf{x_2})|^2 \mathrm{d}^3\mathbf{x_1}\mathrm{d}^3\mathbf{x_2} \tag{8.5.9}$$

Assume for simplicity that the electrons are non interacting so that the Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2_{\mathbf{x_1}} + V(\mathbf{x_1}) - \frac{\hbar^2}{2m}\nabla^2_{\mathbf{x_2}} + V(\mathbf{x_2})\right]\Psi = E\Psi \tag{8.5.10}$$

is separable, so there is a solution of the form $\psi_A(\mathbf{x_1})\psi_B(\mathbf{x_2})$ with

$$\int \mathrm{d}^3\mathbf{x}\,|\psi_A(\mathbf{x})|^2 = 1\,, \qquad \int \mathrm{d}^3\mathbf{x}\,|\psi_B(\mathbf{x})|^2 = 1\,, \qquad \int \mathrm{d}^3\mathbf{x}\,\psi^*_A(\mathbf{x})\psi_B(\mathbf{x}) = \alpha_{AB} \neq 0 \tag{8.5.11}$$

By Schwarz's inequality $|\langle u, v\rangle| \leq \sqrt{\langle u, u\rangle}\sqrt{\langle v, v\rangle}$ we have

$$\int \mathrm{d}^3\mathbf{x}\, \psi_A^*(\mathbf{x})\psi_B(\mathbf{x}) = |\langle \psi_A, \psi_B\rangle| \leq \sqrt{|\langle \psi_A, \psi_A\rangle|}\sqrt{|\langle \psi_B, \psi_B\rangle|} \implies \boxed{|\alpha_{AB}| \leq 1} \tag{8.5.12}$$

But then must build

$$\phi_\pm(\mathbf{x_1}, \mathbf{x_2}) = \frac{N_\pm}{\sqrt{2}}\big(\psi_A(\mathbf{x_1})\psi_B(\mathbf{x_2}) \pm \psi_A(\mathbf{x_2})\psi_B(\mathbf{x_1})\big) \tag{8.5.13}$$

with $N_\pm$ a real normalization constant.

Take the following combination of ϕ and χ:

$\phi_+ \cdot \chi_{\text{singlet}}$	so that the total wavefunction is antisymmetric
$\phi_- \cdot \chi_{\text{triplet}}$	any of the 3 states of the triplet

Again, the probability to find one electron in $\mathrm{d}^3\mathbf{x_1}$ around $\mathbf{x_1}$ and in $\mathrm{d}^3\mathbf{x_2}$ around $\mathbf{x_2}$ is

$$\begin{aligned}\mathrm{d}P_\pm &= |\phi_\pm(\mathbf{x_1}, \mathbf{x_2})|^2 \mathrm{d}^3\mathbf{x_1}\mathrm{d}^3\mathbf{x_2} \\ &= \frac{N_\pm}{\sqrt{2}}\Big\{|\psi_A(\mathbf{x_1})\psi_B(\mathbf{x_2}|^2 + |\psi_A(\mathbf{x_2})\psi_B(\mathbf{x_1})|^2 \pm \underbrace{2\Re\big[\psi_A^*(\mathbf{x_1})\psi_A(\mathbf{x_2})\psi_B^*(\mathbf{x_2})\psi_B(\mathbf{x_1})\big]}_{\text{Exchange density}}\Big\}\mathrm{d}^3\mathbf{x_1}\mathrm{d}^3\mathbf{x_2}\end{aligned} \tag{8.5.14}$$

If we take the case $\mathbf{x_1} = \mathbf{x_2} = \mathbf{x}$, we get

$$\begin{aligned} &\mathrm{d}P_\pm = N_\pm\Big\{|\psi_A(\mathbf{x})\psi_B(\mathbf{x})|^2 \pm |\psi_A(\mathbf{x})\psi_B(\mathbf{x})|^2\Big\}\mathrm{d}^3\mathbf{x_1}\mathrm{d}^3\mathbf{x_2} \\ \implies\ &\mathrm{d}P_+ = 2N_\pm|\psi_A(\mathbf{x})\psi_B(\mathbf{x})|^2\mathrm{d}^3\mathbf{x_1}\mathrm{d}^3\mathbf{x_2} \qquad (8.5.15) \\ &\mathrm{d}P_- = 0 \qquad (8.5.16)\end{aligned}$$

Recall that P_+ is associated with the singlet, while P_- with the triplet. Therefore electrons avoid each other in space when they are in the triplet state. In the singlet states there is enhanced probability to be at the same point.
Note that normalization requires

$$\begin{aligned}1 &= \frac{N_\pm^2}{2}\int \mathrm{d}^3\mathbf{x_1}\mathrm{d}^3\mathbf{x_2}\left\{|\psi_A(\mathbf{x_1})\psi_B(\mathbf{x_2}|^2 + |\psi_A(\mathbf{x_2})\psi_B(\mathbf{x_1})|^2 \pm 2\Re\big[\psi_A^*(\mathbf{x_1})\psi_A(\mathbf{x_2})\psi_B^*(\mathbf{x_2})\psi_B(\mathbf{x_1})\big]\right\} \\ &= \frac{N_\pm^2}{2}\left\{1 + 1 \pm 2\Re\left[\int \mathrm{d}^3\mathbf{x_1}\,\psi_A^*(\mathbf{x_1})\psi_B(\mathbf{x_1})\int \mathrm{d}^3\mathbf{x_2}\,\psi_B^*(\mathbf{x_2})\psi_A(\mathbf{x_2})\right]\right\} \\ &= N_\pm^2\Big\{1 \pm \Re\left[\alpha_{AB}\cdot\alpha_{AB}^*\right]\Big\} \\ &= N_\pm^2\Big(1 \pm |\alpha_{AB}|^2\Big) \implies \boxed{N_\pm = \frac{1}{\sqrt{1 \pm |\alpha_{AB}|^2}}}\end{aligned} \tag{8.5.17}$$

So

$$\mathrm{d}P_+ = \frac{2}{1 \pm |\alpha_{AB}|^2} |\psi_A(\mathbf{x})\psi_B(\mathbf{x})|^2 \mathrm{d}^3\mathbf{x_1}\mathrm{d}^3\mathbf{x_2} \tag{8.5.18}$$

to be compared with

$$\mathrm{d}P_D = |\psi_A(\mathbf{x})|^2 |\psi_B(\mathbf{x})|^2 \mathrm{d}^3\mathbf{x_1}\mathrm{d}^3\mathbf{x_2} \tag{8.5.19}$$

for distinguishable particles.
Since from (8.5.12) we have $|\alpha_{AB} < 1|$, then

$$\mathrm{d}P_+ \geq \mathrm{d}P_D \tag{8.5.20}$$

Assume $\psi_A(\mathbf{x})$ is nonzero only in a region R_A, $\psi_B(\mathbf{x})$ is nonzero only in a region R_B and $R_A \cap R_B = 0$, then

$$\alpha_{AB} = \int \mathrm{d}^3\mathbf{x}\, \psi_A^*(\mathbf{x})\psi_B(\mathbf{x}) = 0 \tag{8.5.21}$$

since ψ_A requires $\mathbf{x} \in R_A$ and ψ_B requires $\mathbf{x} \in R_B$. Therefore in this case $N_\pm = 1$.
Then the probability to find an electron in $\mathrm{d}^3\mathbf{x_1}$ around $\mathbf{x_1} \in R_A$ and another in $\mathrm{d}^3\mathbf{x_2}$ around $\mathbf{x_2} \in R_B$ is

$$\begin{aligned}\mathrm{d}P_\pm &= \Big\{ |\psi_A(\mathbf{x_1})\psi_B(\mathbf{x_2}|^2 + |\cancel{\psi_A(\mathbf{x_2})\psi_B(\mathbf{x_1})}|^2 \pm 2\Re\big[\psi_A^*(\mathbf{x_1})\cancel{\psi_A(\mathbf{x_2})}\psi_B^*(\mathbf{x_2})\cancel{\psi_B(\mathbf{x_1})}\big] \mathrm{d}^3\mathbf{x_1}\mathrm{d}^3\mathbf{x_2} \\ &= |\psi_A(\mathbf{x})|^2 |\psi_B(\mathbf{x})|^2 \mathrm{d}^3\mathbf{x_1}\mathrm{d}^3\mathbf{x_2} = \mathrm{d}P_D \end{aligned} \tag{8.5.22}$$

it is the probability density for distinguishable particles.
Therefore, there is no need to symmetrize or antisymmetrize the wavefunction of non overlapping localized particles.

8.6 Counting states and distributions

E_i energy of the i-th level, d_i degeneracy of the i-th level. Assume we have N particles and we want to place N_1 particles in level 1, ..., N_i particles in level i (E_i, d_i). Let's call $Q(N_1, N_2, \dots)$ the number of ways to do this.

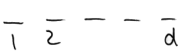
8.6.1 Distinguishable particles (Maxwell Boltzman)

Split N into $N_1, N_2, \dots$ in $\frac{N!}{N_1!N_2!\dots}$ ways (imagine putting them on a line $\underbrace{\dots}_{N_1}\underbrace{\dots}_{N_2}$ after drawing one ball at a time). Placing N_i particles in d_i slots gives $(d_i)^{N_i}$ ways, therefore

$$\boxed{Q(N_1, N_2, \dots) = N! \prod_i \frac{(d_i)^{N_i}}{N_i!}} \qquad \text{Maxwell Boltzman}$$

8.6.2 Identical fermions

Splitting the N states into groups for identical particles can only be done in one way



$N_i < d_i$

how many ways to place them?

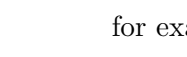
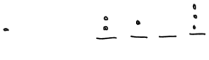
$$d_i \text{ choose } N_i = \frac{d_i}{N_i!(d_i - N_i)!}$$

$$\implies Q(N_1, N_2, \dots) = \prod_i \frac{d_i}{N_i!(d_i - N_i)!}$$

8.6.3 Identical bosons

N_i particles!

N_i balls and $(d_i - 1)$ bars,

for example:  

How many ways to order the $N_i + d_i - 1$ objects? $(N_i + d_i - 1)!$ but we must divide by the irrelevant permutations, hence

$$Q(N_1, N_2, \dots) = \prod_i \frac{(N_i + d_i - 1)!}{N_i!(d_i - 1)!} \tag{8.6.1}$$

This is for bosons:
$Q(N_1, N_2, \dots)$ counts the number of ways to have N particles and fixed energy $E = \sum_i N_i E_i$. Want to find the values of $N_1, N_2, \dots$ that are most likely.
Want to maximize $Q(N_1, N_2, \dots)$ under the constraint that $N = \sum_i N_i$ and $E = \sum_i N_i E_i$.
Maximizing Q is the same as maximizing $\ln Q$ and using lagrange multipliers

$$f(N_1, N_2, \dots) = \ln Q(N_1, N_2, \dots) + \alpha(N - \sum_i N_i) + \beta(E - \sum_i N_i E_i) \tag{8.6.2}$$

Do the fermion one, using Q_F from (8.6.1) we have

$$\ln Q_F = \sum_i \ln d_i! - \ln N_i! - \ln(d_i - N_i)! \tag{8.6.3}$$

Since all these quantities d_i, N_i are large we can use the Stirling approximation

$$\ln n! \simeq n \ln n - n \tag{8.6.4}$$

so that

$$\ln Q_F = \sum_i d_i \ln d_i \cancel{-d_i} - N_i \ln N_i \cancel{+N_i} - (d_i - N_i)\ln(d_i - N_i) \cancel{+d_i - N_i} = \sum_i d_i \ln d_i - N_i \ln N_i - (d_i - N_i)\ln(d_i - N_i) \tag{8.6.5}$$

Minimizing w.r.t. to N_i without constraints,

$$\frac{\mathrm{d}}{\mathrm{d}N_i} \ln Q_F = -\ln N_i \cancel{-1} + \ln(d_i - N_i) \cancel{+1} = \ln\left(\frac{d_i - N_i}{N_i}\right). \tag{8.6.6}$$

so that, adding the lagrange multipliers, we have

$$\frac{\partial f}{\partial N_i} = \ln\left(\frac{d_i - N_i}{N_i}\right) - \alpha - \beta E_i \implies \frac{d_i - N_i}{N_i} = e^{\alpha + \beta E_i} \implies d_i = N_i\left(e^{\alpha+\beta E_i} + 1\right)$$

$$\implies N_i = \frac{d_i}{e^{\alpha+\beta E_i} + 1} \tag{8.6.7}$$

α and β can be calculated using the equations $\sum_i N_i = N$ and $\sum_i N_i E_i = E$:

$$\alpha \equiv -\frac{\mu(T)}{k_B T}, \qquad \beta \equiv \frac{1}{k_B T} \quad \text{definition of temperature} \tag{8.6.8}$$

then

$$N_i = \frac{d_i}{e^{\frac{E_i - \mu(T)}{k_B T}} + 1} \tag{8.6.9}$$

The expected occupation number $n \sim \frac{N_i}{d_i}$ for a single state is

$$\boxed{n = \left(e^{\frac{E-\mu(T)}{k_B T}} + 1\right)^{-1}} \qquad \text{Fermi-Dirac distribution}$$

For bosons we have

$$\boxed{n = \left(e^{\frac{E-\mu(T)}{k_B T}} - 1\right)^{-1}} \qquad \text{Bose-Einstein distribution}$$

Since $n \geq 0$ we need $E > \mu$ for all energy levels $\mu < E_i \ \forall i$. For an ideal gas $\mu(T) < 0 \ \forall T$, i.e. $\alpha > 0$

For fermions

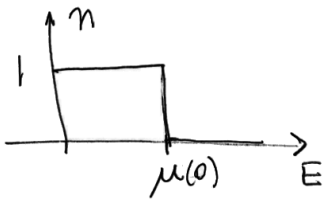


Figure 8.3: Occupation number for a state as a function of the energy for a system of identical fermions in the $T \to 0$ limit. $\mu(T=0) = E_F$is called the *Fermi energy*.

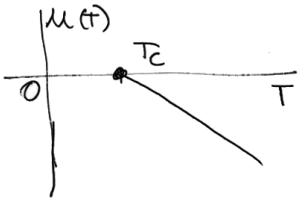


Figure 8.4: Chemical potential μ as a function of the temperature for a system of identical bosons. T_C, the *critical temperature* is defined to be the temperature such that $\mu(T_C) = 0$ and it's the temperature for Bose-Einstein condensation

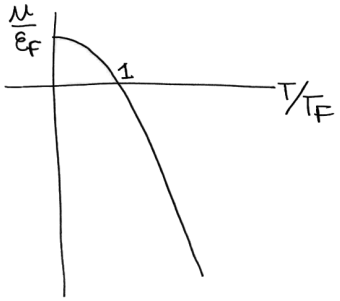


Figure 8.5: Chemical potential μ as a function of the temperature for a system of identical fermions.

Aside from statistical mechanics

$$\mu = \left.\frac{\partial E}{\partial N}\right|_{S,V} \qquad \text{keeping constant entropy may require lowering the energy} \qquad (8.6.10)$$

Suppose we add a particle with no energy to the system. S will increase (more ways to

divide up the total energy) for this not to happen, must reduce the energy.

$$\begin{aligned} \mathrm{d}E(V,S) &= T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N \\ &= \mathrm{d}(TS) - S\mathrm{d}T - P\mathrm{d}V \\ \mathrm{d}\underbrace{(E-TS)} &= -S\mathrm{d}T - P\mathrm{d}V + \mu\mathrm{d}N \end{aligned} \tag{8.6.11}$$

$$F(T,V) = E - TS\,. \tag{8.6.12}$$

μ is an intensive quantity, and in terms of F we have

$$\mu = \left.\frac{\partial F}{\partial N}\right|_{T,V} \qquad \begin{array}{c}\text{Adding a particle changes}\\ \text{the energy and the entropy}\end{array} \tag{8.6.13}$$